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THEORETICAL CHEMISTRY OF THE 7p SERIES OF SUPERHEAVY ELEMENTS II.† THE RELATIVISTIC MOLECULAR ORBITAL AND KAPPA VALENCE METHODS

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The relativistic generalizations of both molecular orbital and spin-valence (the Kappa valence method) theories are used to investigate the covalent bonds that can be formed by the ground relativistic configuration of a heavy element containing a non-closed subshell of $\bar{p}$ or p valence electrons.

Both theories predict that $\bar{p}$–H and p–H bonds are not greatly weakened compared with normal covalent σ bonds and that covalent compounds based on the p^2 relativistic configuration will be bent with an equilibrium interbond angle of 90°. Both $\bar{p}$–H and p–H bonds are predicted by the Kappa valence method to be a mixture of a normal covalent σ bond and the triplet bond formed by the interaction of two electrons occupying orthogonal orbitals. This method predicts that the bond formed between a heavy element and a group of rather different electronegativity may be weakened by relativity more than a $\bar{p}$–H or p–H bond because only the non-orthogonal Heitler–London singlet portion of such a bond can be stabilized by ionic–covalent resonance.

The Kappa valence method is used to show that a closed $\bar{p}^2$ subshell cannot form a stable covalent bond.

Both Kappa valence and relativistic molecular orbital methods are used to investigate the bonding between an element having a single $\bar{p}$ or p valence electron and a group containing both a closed shell of π electrons and a single electron in the σ orbital. It is shown by the Kappa valence method that the presence of the π electrons introduces destabilizing anti-bonding terms unless the π–σ excitation energy is small as for a halogen. The destabilizing term is predicted to inhibit the formation of a normal covalent bond between a $\bar{p}$ orbital and such a group while in the p case the bond is merely predicted to be greatly weakened. In the case for which the π–σ excitation energy is small both Kappa valence and relativistic molecular orbital theories predict that the bond is not weakened because the group adopts a valence state that eliminates the anti-bonding terms to yield a bond of unit order containing both σ and π character. It is shown by the Kappa valence method that the ionic-covalent resonance stabilizations of $\bar{p}$–Halogen and p–Halogen bonds are not qualitatively dissimilar to that of the corresponding non-relativistic bond. Relativistic molecular orbital theory is used to show that the ground manifold of an element having two valence electrons occupying Dirac–Fock p orbitals can covalently bind two halogens and that the potential energy curve for inter-bond angle bending is shallow.

The bonding between the *j–j* coupled ground states of two heavy elements each containing a single valence electron occupying a $\bar{p}$ or a p Dirac–Fock atomic orbital is investigated by both the Kappa valence and relativistic molecular orbital methods. It is shown that $\bar{p}$–$\bar{p}$ but not $\bar{p}$–p bonds are greatly weakened by relativity and that p–p bonds are entirely π in character. These results are used to comment on the cohesive energies of elemental E113 and E115.

1. Introduction

The overall objective of the series of three papers (Pyper & Grant (1981*a*), paper I, the present work and Pyper (1982), paper III), of which this paper constitutes the second member, is to predict the theoretical chemistry of the 7p series of superheavy elements. The purpose of this second paper is to investigate the nature of the covalent bonds that can be formed by the ground state of a superheavy element whose most loosely bound electrons occupy $\bar{p}$ or p Dirac–Fock atomic orbitals.

The occupation of $\bar{p}$ or p orbitals introduces new factors into the chemistry of such elements because the directional properties of the large components of relativistic Dirac–Fock atomic orbitals, excepting those of s symmetry and those whose m_j quantum numbers (Grant 1970) equal $\pm j$, are quite different from those of the non-relativistic atomic orbitals conventionally used to describe chemical bonding (Pitzer 1975). Only a linear combination of the two such Dirac–Fock orbitals that have the same principal quantum number and orbital angular momentum (l) associated with the large components but different total angular momenta $j\ (= l \pm \frac{1}{2})$ produces an orbital whose large components have the same directional and spin properties as a non-relativistic spatial orbital occupied by an electron having a definite z-spin component. For light elements, the energy needed to promote the *j–j* coupled ground state of an atom containing a single electron in a $\bar{p}$ or a p Dirac–Fock atomic orbital to a valence state capable of forming a normal covalent singlet bond is small compared with chemical binding energies. Hence taking z to be the internuclear axis, the bond between a light element and a group containing a single unpaired electron in a σ orbital will be well described by the relativistic valence bond wavefunction. This is the direct relativistic analogue, built from four-component orbitals whose large components correspond to the spin-orbitals $p_z\alpha$ and $p_z\beta$, of the Heitler–London wavefunction (Pyper 1980*a*).

The valence state excitation energies for the 7p series of superheavy elements are, however, so large that they are predicted (Pitzer 1975, Grant & Pyper 1977, see also paper III) to inhibit greatly the formation of chemical bonds of the conventional relativistic valence bond type. This paper answers the question which therefore naturally arises as to whether the ground state of such a heavy element can form a covalent bond without invoking a valence state in which electrons are partially promoted from $\bar{p}$ into p orbitals. This is achieved by first examining the nature of the bonds that can be formed between the ground relativistic configuration of a superheavy element and an atom or group containing one unpaired electron occupying a σ orbital but no valence π electrons. Second the study is extended to examine how the conclusions are modified by the presence of valence π electrons on the bonded group.

The study reported in §3 examining the bonding between a heavy element and a group containing no valence π electrons not only fills in the details of the preliminary accounts (Pyper 1980*a*, *b*), which used the Kappa valence method, of the bonding to a hydrogen atom but also shows that the relativistic version of molecular orbital theory makes very similar predictions. This study is then extended, by using both the Kappa valence and relativistic molecular orbital approaches, to investigate the covalent bonding between two hydrogen atoms and a heavy element having two valence electrons occupying p Dirac–Fock atomic orbitals. The Kappa valence wavefunction for such a system is taken to be that function yielding the strongest bond subject to the proviso that $\bar{p}$ electrons are not promoted into p orbitals. The excitation energy between the p_2^2 and p_0^2, where the subscript denotes the total angular momentum J (Grant 1970), levels of the relativistic p^2 configuration is assumed in this approach to be negligible compared with chemical binding energies. Thus the method, which can be called the J-valence method, in which the wavefunction is constructed by vector coupling two relativistic hydrogen-1s orbitals to the ground p_2^2 level of the heavy element is not considered. Finally the Kappa valence method is used to show that a closed $\bar{p}^2$ subshell cannot form covalent bonds.

The last three sections of this paper examine how the conclusions of §§3, 4 and 5 are modified by the presence of π electrons in the valence shell of the atom or group to which the heavy element is bonded. This is achieved by first investigating, by both the Kappa valence and relativistic molecular orbital methods, the purely covalent bonding between a halogen and the *j–j* coupled ground state of a heavy element containing a single electron in a Dirac–Fock $\bar{p}$ or p orbital. The relativistic molecular orbital method is then used to show that a heavy element containing two valence electrons occupying a Dirac–Fock p orbital can covalent bind two halogens in a manner exactly analogous to the binding of a single halogen to an element containing a single $\bar{p}$ or p valence electron. The investigation is completed by investigating the covalent bonding between the *j–j* coupled ground states of a pair of heavy elements each having a single $\bar{p}$ or p valence electron. The conclusions of some of this research have been published recently (Pyper 1980*b*).

2. The symmetry properties of multi-electron relativistic wavefunctions

(a) *The hamiltonian*

The group theoretical properties of the relativistic analogue of the multi-electron Schrödinger equation will be derived because approximate wavefunctions having the correct symmetry are usually more trustworthy than non-symmetry-adapted approximations. This discussion differs from that of Oreg & Malli (1974) not only in that the full Brown hamiltonian including projection operators is examined but also in that it is perhaps more straightforward because it proceeds by directly seeking operators that commute with the Brown hamiltonian.

The closest relativistic analogue of the non-relativistic Schrödinger equation for an N-electron system is the equation determining the eigenkets $(|\psi_\alpha(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)\rangle)$ and energies (E_α) of the Brown hamiltonian $(\hat{\mathscr{H}}_{\mathrm{Br}})$ (Brown & Ravenhall 1951, Mittleman 1972)

$$\hat{\mathscr{H}}_{\mathrm{Br}}|\psi_\alpha(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)\rangle = \hat{\mathscr{P}}^{(+)}\hat{\mathscr{H}}_{\mathrm{T}}\hat{\mathscr{P}}^{(+)}|\psi_\alpha(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)\rangle = E_\alpha|\psi_\alpha(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)\rangle \tag{2.1}$$

with

$$\hat{\mathscr{H}}_{\mathrm{T}} = \sum_{i=1}^{N}\hat{\mathscr{H}}_{\mathrm{D}}(i) + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} r_{ij}^{-1}, \tag{2.2}$$

$$\hat{\mathscr{H}}_{\mathrm{D}}(i) = c\boldsymbol{\alpha}(i)\cdot\hat{\mathbf{p}}(i) + c^2[\beta(i) - 1] + \hat{V}_{\mathrm{nuc}}(\boldsymbol{r}_i) \tag{2.3}$$

$$\equiv \hat{\mathscr{H}}_{\mathrm{k.e.}}(i) + \hat{V}_{\mathrm{nuc}}(\boldsymbol{r}_i), \tag{2.4}$$

$$\hat{\mathscr{P}}^{(+)} = \sum_{r^{(+)}} |\Phi_r^{(+)}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)\rangle\langle\Phi_r^{(+)}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)|. \tag{2.5}$$

The operator (2.2), which is expressed in atomic units, is the most obvious generalization of the non-relativistic hamiltonian in which the Schrödinger kinetic energy operator for the ith electron is replaced by the Dirac one $\hat{\mathscr{H}}_{\mathrm{k.e.}}(i)$. In the operator $\hat{\mathscr{H}}_{\mathrm{D}}(i)$ which acts solely on the coordinates of electron i, the zero of energy is defined to correspond to that of a stationary free electron, $\hat{\mathbf{p}}(i)$ and $\hat{V}_{\mathrm{nuc}}(\boldsymbol{r}_i)$ are operators for momentum, and the potential energy of interaction with nuclei, which are regarded as stationary spherically symmetric distributions of positive charge possessing no magnetic moments, and c is the velocity of light. The quantities $\boldsymbol{\alpha}$ and β are 4×4 Dirac matrices

$$\boldsymbol{\alpha} = \begin{bmatrix} 0 & \boldsymbol{\sigma}^{\mathrm{P}} \\ \boldsymbol{\sigma}^{\mathrm{P}} & 0 \end{bmatrix}, \quad \beta = \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix} \tag{2.6}$$

where $\boldsymbol{\sigma}^{\mathrm{P}}$ are the 2×2 Pauli matrices and I is a 2×2 identity matrix (Dirac 1958). The operators $\hat{\mathscr{P}}^{(+)}$ are projection operators onto the subspace spanned by the infinite number of antisymmetrized N-electron Hartree products

$$|\Phi_r^{(+)}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)\rangle = \hat{\mathscr{A}}\left\{\prod_{i=1}^{N}|\phi_{a_i}(\boldsymbol{r}_i)\rangle\right\} \tag{2.7}$$

that can be constructed from the solutions $|\phi_a(\boldsymbol{r})\rangle$ of the Dirac–Fock equation

$$\hat{\mathrm{F}}|\phi_a(\boldsymbol{r})\rangle = (\hat{\mathscr{H}}_{\mathrm{k.e.}} + \hat{V}_{\mathrm{nuc}} + \hat{V}_{\mathrm{el}})\,|\phi_a(\boldsymbol{r})\rangle = \epsilon_a|\phi_a(\boldsymbol{r})\rangle \tag{2.8}$$

which have energies $\epsilon_a > -2c^2$ and therefore describe electrons. The operator $\hat{\mathscr{H}}_{\mathrm{Br}}$ is not unique because the orbitals $|\phi_a\rangle$ used to construct the $\hat{\mathscr{P}}^{(+)}$ are defined by (2.8) which contains the potential $\hat{V}_{\mathrm{el}}$ which can be chosen in a variety of ways. However a full quantum electrodynamic calculation in which both the electron-like and positron-like solutions of (2.8) were considered would yield the same result no matter how $\hat{V}_{\mathrm{el}}$ was chosen.

The Brown hamiltonian is only an approximation to the complete description provided by quantum electrodynamics not only because it neglects effects of the solutions of (2.8) having $\epsilon_a < -2c^2$, which describe positrons, but also because the r_{ij}^{-1} terms in (2.2) are not Lorentz covariant. However, the results of relativistic atomic calculations (Desiderio & Johnson 1971) have shown that even the leading corrections arising from the positron-like solutions of (2.8), namely the vacuum polarization and self-energy terms (of order $1/c^3$, compared with $1/c^2$ for relativistic effects), are only a small fraction of ϵ_a if $\hat{V}_{\mathrm{el}}$ is chosen to be the Dirac–Fock potential generated by the occupied atomic orbitals. Hence the corrections to (2.1) arising from electron–positron pair creation are negligible for valence electrons provided $\hat{V}_{\mathrm{el}}$ is chosen in a physically sensible way. For valence electrons, the errors caused by the non-covariance of the r_{ij}^{-1} terms are negligible compared with chemical bond energies because addition of the Breit hamiltonian to (2.2), which rectifies this to lowest order in $1/c^2$, only changes valence electron energies by a few hundred cm^{-1} in heavy atoms (Mann & Johnson 1971).

(*b*) *Linear triatomic molecules*

(i) *Symmetry properties of the Fock hamiltonian*

The symmetry properties of wavefunctions for linear triatomic molecules of the type AB_2 will first be derived because they are closely related to those of the other systems studied, namely linear diatomic and bent AB_2 molecules. The coordinate system used, which is a right-handed one centred on atom A with z taken along the internuclear axis, is shown in figure 1.

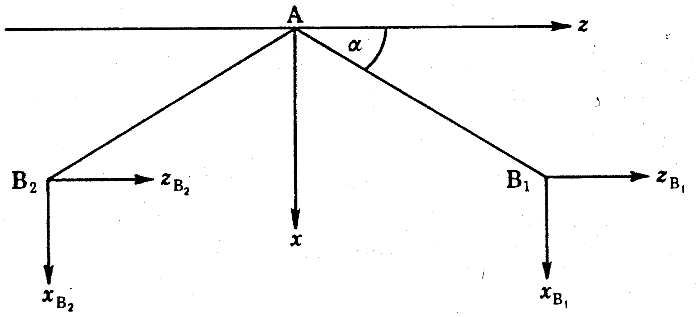

FIGURE 1. The coordinate system. A, B_1 and B_2 label the nuclei A, B_1 and B_2 respectively. All three y-axes, y, y_{B_1} and y_{B_2} are oriented perpendicular and into the plane of the paper.

The symmetry properties of the Fock hamiltonian (2.8) are first investigated since those of the Brown hamiltonian (2.1) are closely related not only because they both contain the Dirac kinetic energy operator but also because the eigenfunctions $|\phi_a(r)\rangle$ of $\hat{\mathrm{F}}$ are used to construct $\mathscr{H}_{\mathrm{Br}}$. The one-electron operator $\hat{\mathrm{l}}_z(i)$ corresponding to the z-component of the orbital angular momentum, that, $\hat{\mathrm{I}}_{\mathrm{s}}(i)$, corresponding to spatial inversion and those, $\hat{\mathrm{H}}_{x,\mathrm{s}}(i)$, $\hat{\mathrm{H}}_{y,\mathrm{s}}(i)$ and $\hat{\mathrm{H}}_{z,\mathrm{s}}(i)$, corresponding to spatial reflexions in the yz-, xz- and xy-planes, obey

$$[\hat{\mathrm{l}}_z, (\hat{V}_{\mathrm{nuc}}+\hat{V}_{\mathrm{el}})] = [\hat{\mathrm{I}}_{\mathrm{s}}, (\hat{V}_{\mathrm{nuc}}+\hat{V}_{\mathrm{el}})] = [\hat{\mathrm{H}}_{q,\mathrm{s}}, (\hat{V}_{\mathrm{nuc}}+\hat{V}_{\mathrm{el}})] = 0, \quad q = x, y, z, \tag{2.9}$$

provided the electronic potential $\hat{V}_{\mathrm{el}}$ is chosen to have the full symmetry of the nuclear framework. It would introduce unnecessary complications not to chose $\hat{V}_{\mathrm{el}}$ such that the relations (2.9) are satisfied even though this choice implies that the orbitals used to construct one component of any electronically degenerate state cannot be eigenfunctions of a fully self-consistent Dirac–Fock potential but only of an operator constructed from the average of all the degenerate components. Such an average Fock operator is the relativistic analogue of that used to define the orbitals in the non-relativistic restricted Hartree–Fock description of an open-shell atom (Roothaan 1960). It is well known that the $c\boldsymbol{\alpha}\cdot\hat{\mathbf{p}}$-term in the Dirac kinetic energy operator prevents $\hat{\mathrm{F}}$ from commuting with any of the operators $\hat{\mathrm{I}}_z$, $\hat{\mathrm{I}}_{\mathrm{s}}$, $\hat{\mathrm{H}}_{x,\mathrm{s}}$, $\hat{\mathrm{H}}_{y,\mathrm{s}}$ or $\hat{\mathrm{H}}_{z,\mathrm{s}}$, which correspond to the elements of the spatial symmetry group of the molecule, because for example $c\boldsymbol{\alpha}\cdot\hat{\mathbf{p}}$ is changed to $c(-\alpha_x \mathrm{p}_x+\alpha_y \mathrm{p}_y+\alpha_z \mathrm{p}_z)$ and $-c\boldsymbol{\alpha}\cdot\hat{\mathbf{p}}$ respectively under the action of $\hat{\mathrm{H}}_{x,\mathrm{s}}$ and $\hat{\mathrm{I}}_{\mathrm{s}}$ which change x, y, z to $-x$, y, z and $-x$, $-y$, $-z$ respectively. Thus using the passive mode in which symmetry operations are represented by transformations of the coordinate frame (Brink & Satchler 1962), one has

$$\left.\begin{aligned}\hat{\mathrm{I}}_{\mathrm{s}}^{-1}\hat{\mathrm{F}}\hat{\mathrm{I}}_{\mathrm{s}} &= -c\boldsymbol{\alpha}\cdot\hat{\mathbf{p}}+c^2(\beta-1)+\hat{V}_{\mathrm{nuc}}+\hat{V}_{\mathrm{el}},\\ \hat{\mathrm{H}}_{q,\mathrm{s}}^{-1}\hat{\mathrm{F}}\hat{\mathrm{H}}_{q,\mathrm{s}} &= c(-\alpha_q\hat{\mathrm{p}}_q+\sum_{q'\neq p}\alpha_{q'}\hat{\mathrm{p}}_{q'})+c^2(\beta-1)+\hat{V}_{\mathrm{nuc}}+\hat{V}_{\mathrm{el}}.\end{aligned}\right\} \tag{2.10}$$

However, by introducing appropriate 4 × 4 matrices, it is possible to construct transformations derived from the spatial symmetry operations that both commute with $\hat{\mathrm{F}}$ and reflect faithfully the group multiplication table. Introducing the 4 × 4 matrices

$$\Sigma_q = \begin{bmatrix}\sigma_q^{\mathrm{P}} & 0\\ 0 & \sigma_q^{\mathrm{P}}\end{bmatrix} \tag{2.11}$$

whose squares are unity, defining

$$\hat{\mathrm{j}}_z = \hat{\mathrm{I}}_z+\tfrac{1}{2}\Sigma_z,\quad \hat{\mathrm{I}}_{\mathrm{t}} = \mathrm{I}_{\mathrm{u}}\hat{\mathrm{I}}_{\mathrm{s}},\quad \hat{\mathrm{H}}_{q,\mathrm{t}} = \hat{\mathrm{H}}_{q,\mathrm{u}}\mathrm{H}_{q,\mathrm{s}},\quad q = x, y, z, \tag{2.12}$$

where

$$\mathrm{I}_{\mathrm{u}} = \beta,\quad \mathrm{H}_{q,\mathrm{u}} = \mathrm{i}\Sigma_q\beta,\quad q = x, y, z, \tag{2.13}$$

obeying

$$\mathrm{I}_{\mathrm{u}}^{-1} = \beta,\quad \mathrm{H}_{q,\mathrm{u}}^{-1} = -\mathrm{i}\Sigma_q\beta,\quad q = x, y, z, \tag{2.14}$$

and noting that $\Sigma_i = -\mathrm{i}\epsilon_{ijk}\alpha_j\alpha_k$ with ϵ_{ijk} the antisymmetric three-index symbol (Margenau & Murphy 1964), one can readily show using the anticommutation relations satisfied by the matrices α_x, α_y, α_z and β that

$$\hat{\mathrm{I}}_{\mathrm{t}}^{-1}\hat{\mathrm{F}}\hat{\mathrm{I}}_{\mathrm{t}} = \hat{\mathrm{H}}_{q,\mathrm{t}}^{-1}\hat{\mathrm{F}}\hat{\mathrm{H}}_{q,\mathrm{t}} = \hat{\mathrm{F}}. \tag{2.15}$$

The commutator of $\hat{\mathrm{F}}$ with $\hat{\mathrm{j}}_z$ is standard while those with $\hat{\mathrm{I}}_{\mathrm{t}}$ and $\hat{\mathrm{H}}_{q,\mathrm{t}}$ follow immediately from (2.15), so that

$$[\hat{\mathrm{F}}, \hat{\mathrm{j}}_z] = [\hat{\mathrm{F}}, \hat{\mathrm{I}}_{\mathrm{t}}] = [\hat{\mathrm{F}}, \hat{\mathrm{H}}_{q,\mathrm{t}}] = 0,\quad q = x, y, z. \tag{2.16}$$

The choice made for the phases of the operators (2.13), which are determined by demanding that the operators satisfy the group multiplication table, is justified in Appendix 1.

The eigenvalues, denoted i_{p}, of the operator $\hat{\mathrm{I}}_{\mathrm{t}}$ are ± 1 and those, denoted h_q, of $\hat{\mathrm{H}}_{q,\mathrm{t}}$ are $\pm\mathrm{i}$ because $\hat{\mathrm{I}}_{\mathrm{t}}^2 = 1$ and $\hat{\mathrm{H}}_{q,\mathrm{t}}^2 = -1$. The eigenfunctions $|\phi_a(\boldsymbol{r})\rangle$ of $\hat{\mathrm{F}}$ (equation (2.8)) can be chosen to be simultaneous eigenfunctions of $\hat{\mathrm{j}}_z$, $\hat{\mathrm{I}}_{\mathrm{t}}$ and $\hat{\mathrm{H}}_{z,\mathrm{t}}$ also and therefore written as $|\phi_a m i_{\mathrm{p}} h_z\rangle$, where m is the $\hat{\mathrm{j}}_z$-eigenvalue, because these three operators not only commute with $\hat{\mathrm{F}}$ but also with each other. Thus

$$\hat{\mathrm{j}}_z|\phi_a m i_{\mathrm{p}} h_z\rangle = m|\phi_a m i_{\mathrm{p}} h_z\rangle, \tag{2.17a}$$

$$\hat{\mathrm{H}}_{z,\mathrm{t}}|\phi_a m i_{\mathrm{p}} h_z\rangle = h_z|\phi_a m i_{\mathrm{p}} h_z\rangle, \tag{2.17b}$$

$$\hat{\mathrm{I}}_{\mathrm{t}}|\phi_a m i_{\mathrm{p}} h_z\rangle = i_{\mathrm{p}}|\phi_a m i_{\mathrm{p}} h_z\rangle. \tag{2.17c}$$

However, the $|\phi_a m i_{\mathrm{p}} h_z\rangle$ are not eigenkets of $\hat{\mathrm{H}}_{x,\mathrm{t}}$ or $\hat{\mathrm{H}}_{y,\mathrm{t}}$ because neither of these two operators commutes with $\hat{\mathrm{j}}_z$ or $\hat{\mathrm{H}}_{z,\mathrm{t}}$. It is shown in Appendix 2 that both the kets $(\hat{\mathrm{H}}_{q,\mathrm{t}}|\phi_a m i_{\mathrm{p}} h_z\rangle,\ q = x, y)$ are eigenkets of $\hat{\mathrm{F}}$ degenerate with $|\phi_a m i_{\mathrm{p}} h_z\rangle$ having respective eigenvalues of the operators

$\hat{j}_z$, $\hat{H}_{z,t}$ and $\hat{I}_t$ of $-m$, $-h_z$ and i_p. This shows that the kets $(\hat{H}_{q,t}|\phi_a m i_p h_z\rangle)$ can differ fror $|\phi_a - m i_p - h_z\rangle$ by at most a phase factor $e^{i\delta_q}$ so that

$$\hat{H}_{q,t}|\phi_a m i_p h_z\rangle = e^{i\delta_q}|\phi_a - m i_p h_z\rangle, \quad q = x, y. \qquad (2.18$$

The case where $m = 0$ does not require consideration because the allowed values of m ar odd half-integral as is well known.

(ii) *Symmetry properties of the Brown hamiltonian*

The symmetry properties of the Brown hamiltonian are investigated by introducing th multi-electron analogues of the operators $\hat{j}_z$, $\hat{I}_t$ and $\hat{H}_{q,t}$:

$$\hat{J}_{z,T} = \sum_{i=1}^{N} \hat{j}_z(i), \quad \hat{I}_T = \prod_{i=1}^{N} \hat{I}_t(i), \quad \hat{H}_{q,T} = \prod_{i=1}^{N} \hat{H}_{q,t}(i), \quad q = x, y, z. \qquad (2.19$$

These operators obey

$$[\hat{J}_{z,T}, \hat{\mathscr{P}}^{(+)}] = [\hat{I}_T, \hat{\mathscr{P}}^{(+)}] = [\hat{H}_{q,T}, \hat{\mathscr{P}}^{(+)}] = 0, \quad q = x, y, z. \qquad (2.20$$

The commutators of $\hat{\mathscr{P}}^{(+)}$ with $\hat{J}_{z,T}$, $\hat{I}_T$ and $\hat{H}_{z,T}$ vanish because the kets (2.7) are eigenke of these three operators since they are built from the orbitals $|\phi_a m i_p h_z\rangle$. The commutators $\hat{\mathscr{P}}^{(+)}$ with $\hat{H}_{q,t}$ $(q = x, y)$ vanish by virtue of the relation $\hat{H}_{q,t}^{-1}\hat{\mathscr{P}}^{(+)}\hat{H}_{q,t} = \hat{H}_{q,T}$ which hol because $(\hat{\mathscr{A}}\Pi_{i=1}^{N}|\phi_a m i_p h_z\rangle)(\langle\phi_a m i_p h_z|\,\Pi_{i=1}^{N}\hat{\mathscr{A}})$ and $(\hat{\mathscr{A}}\,\Pi_{i=1}^{N}|\phi_a - m i_p - h_z\rangle)(\langle\phi_a - m i_p - h$ $\Pi_{i=1}^{N}\hat{\mathscr{A}})$ both occur in $\hat{\mathscr{P}}^{(+)}$ since the commutation relations (2.16) ensure that if $|\phi_a m i_p h_z\rangle$ is a electron-like solution of (2.8) (i.e. having $\epsilon_a > -2c^2$) then $\hat{H}_{q,t}|\phi_a m i_p h_z\rangle$ also has this propert Arguments identical to those used to establish (2.16) taken in conjunction with (2.20) show th

$$[\hat{J}_{z,T}, \mathscr{H}_{Br}] = [\hat{I}_T, \mathscr{H}_{Br}] = [\hat{H}_{q,T}, \mathscr{H}_{Br}] = 0, \quad q = x, y, z, \qquad (2.2$$

and hence that the eigenkets $|\psi_\alpha\rangle$ of $\mathscr{H}_{Br}$ can be taken to be simultaneously eigenkets of $\hat{J}_{z,}$ $\hat{I}_T$ and $\hat{H}_{z,T}$ and therefore written $|\psi_\alpha M I_p H_z\rangle$.

Arguments identical to those used in Appendix 2 to derive (A 2.2) show that

$$\left.\begin{aligned} \hat{H}_{q,T}^{-1}\hat{J}_{z,T}\hat{H}_{q,T} &= -\hat{J}_{z,T}, \\ \hat{H}_{q,T}^{-1}\hat{H}_{z,T}\hat{H}_{q,T} &= (-1)^N\hat{H}_{z,T}, \end{aligned}\right\} \quad q = x, y, \qquad (2.2$$

and hence that

$$\hat{H}_{q,T}|\psi_\alpha M I_p H_z\rangle = e^{i\delta_q}|\psi_\alpha - M I_p((-1)^N H_z)\rangle, \qquad (2.2$$

where $|\psi_\alpha - M I_p((-1)^N H_z)\rangle$ is an eigenket of $\mathscr{H}_{Br}$ degenerate with $|\psi_\alpha M I_p H_z\rangle$. The ca $M = 0$, which can only occur for N even, needs to be considered separately because in th instance the $|\psi_\alpha\rangle$ can be chosen to be simultaneously eigenkets of all the five operators $\hat{J}_z$, $\hat{I}_T$ and $\hat{H}_{q,T}$, $q = x, y, z$. Since it is readily established that $\hat{H}_{q,T}^2 = 1$ for even N, it follov that the eigenvalues are ± 1 and hence that the eigenkets $|\psi_\alpha 0 I_p H_z\rangle$ must either rema unchanged or change sign under the action of $\hat{H}_{x,T}$ and $\hat{H}_{y,T}$.

(*c*) *Diatomic and nonlinear* AB_2 *molecules*

The entire theory of the last section applies unchanged to homonuclear diatomic molecul if the origin of the coordinate system used is placed midway between the two nuclei, with taken along the internuclear axis. The symmetry properties of heteronuclear diatomic molecul differ from those of homonuclear ones only in that $\hat{I}_s$ and $\hat{H}_{z,s}$ no longer commute with $\hat{V}_n$

or $\hat{V}_{\mathrm{el}}$ so that $\hat{\mathrm{I}}_{\mathrm{t}}$ and $\hat{\mathrm{H}}_{z,\mathrm{t}}$ no longer commute with $\hat{\mathrm{F}}$. This shows that the theory presented in §2(b) applies to heteronuclear diatomic molecules provided the labels i_{p}, h_z, I_{p} and H_z are removed from $|\phi_a m i_{\mathrm{p}} h_z\rangle$ and $|\psi_\alpha M I_{\mathrm{p}} H_z\rangle$, and all references to the operators $\hat{\mathrm{I}}_{\mathrm{s}}$, $\hat{\mathrm{I}}_{\mathrm{t}}$, $\hat{\mathrm{I}}_{\mathrm{T}}$, $\hat{\mathrm{H}}_{z,\mathrm{s}}$, $\hat{\mathrm{H}}_{z,\mathrm{u}}$, $\hat{\mathrm{H}}_{z,\mathrm{t}}$ and $\hat{\mathrm{H}}_{z,\mathrm{T}}$ are deleted.

For bent AB_2 molecules, only $\hat{\mathrm{H}}_{z,\mathrm{s}}$ and $\hat{\mathrm{H}}_{y,\mathrm{s}}$ of the five symmetry operators appearing in (2.9) still commute with $\hat{V}_{\mathrm{nuc}}$ and $\hat{V}_{\mathrm{el}}$ if the coordinate system depicted in figure 1 is used, the nuclei being taken to lie in the xz-plane. Hence the theory of §2(b) applies to bent AB_2 molecules only after the labels m, i_{p}, I_{p} and M are removed from the kets $|\phi_a m i_{\mathrm{p}} h_z\rangle$ and $|\psi_\alpha M I_{\mathrm{p}} H_z\rangle$, and all references to operators constructed from $\hat{\mathrm{l}}_z$, $\hat{\mathrm{I}}_{\mathrm{s}}$, $\hat{\mathrm{I}}_{\mathrm{t}}$, $\hat{\mathrm{H}}_{x,\mathrm{s}}$ and $\hat{\mathrm{H}}_{x,\mathrm{u}}$ are deleted. Thus the eigenkets of $\hat{\mathrm{F}}$ and $\mathscr{H}_{\mathrm{Br}}$ are chosen to be eigenkets of $\hat{\mathrm{H}}_{z,\mathrm{t}}$ and $\hat{\mathrm{H}}_{z,\mathrm{T}}$ and carry the respective labels h_z and H_z.

(d) *The transformation properties of Dirac–Fock atomic orbitals*

The action of the operators $\hat{\mathrm{H}}_{q,\mathrm{t}}$ ($q = x, y, z$) on Dirac–Fock atomic orbitals centred on the nuclei must be known before such orbitals can be used to construct approximations having the correct symmetry to the relativistic wavefunctions $|\psi_\alpha(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)\rangle$. The Dirac–Fock atomic orbitals centred on the nuclei (denoted μ) will be written in the standard form (Grant 1970)

$$|u_\mu jm\rangle = \frac{1}{r}\begin{bmatrix} P(r_\mu) & \chi_{\kappa,m}(\theta_\mu, \phi_\mu) \\ iQ(r_\mu) & \chi_{-\kappa,m}(\theta_\mu, \phi_\mu)\end{bmatrix}, \tag{2.24}$$

and are therefore eigenfunctions of eigenvalues $j(j+1)$ and m respectively of the angular momentum operators $\hat{\mathrm{j}}^2_\mu$ and $\hat{\mathrm{j}}_{z,\mu}$ ($\hat{\mathbf{j}}_\mu = \mathbf{l}_\mu + \frac{1}{2}\boldsymbol{\Sigma}$) defined relative to nucleus μ as origin. The axes x_μ, y_μ and z_μ of the coordinate frames centred on the different nuclei (μ) are chosen to be parallel (figure 1). In (2.24), $P(r_\mu)$ and $Q(r_\mu)$ are purely radial functions defined relative to nucleus μ as origin, and $\chi_{\kappa,m}(\theta_\mu, \phi_\mu)$ is a vector coupled space–spin function

$$\chi_{\kappa,m}(\theta_\mu, \phi_\mu) = \sum_{m_{\mathrm{s}}=\pm\frac{1}{2}} \langle l\tfrac{1}{2}(m-m_{\mathrm{s}})\, m_{\mathrm{s}} | jm\rangle\, Y_{l,(m-m_{\mathrm{s}})}(\theta_\mu, \phi_\mu)\, |\tfrac{1}{2}m_{\mathrm{s}}\rangle \tag{2.25}$$

where $Y_{l,m}(\theta_\mu, \phi_\mu)$ is a spherical harmonic having the same origin as $P(r_\mu)$, and $|\frac{1}{2}m_{\mathrm{s}}\rangle$ is a two-component spin function

$$|\tfrac{1}{2}\,\tfrac{1}{2}\rangle = \begin{bmatrix}1\\0\end{bmatrix} \equiv |\alpha\rangle, \quad |\tfrac{1}{2}\,-\tfrac{1}{2}\rangle = \begin{bmatrix}0\\1\end{bmatrix} \equiv |\beta\rangle. \tag{2.26}$$

The total angular momentum j and orbital angular momentum l associated with the large components are uniquely defined by the quantum number κ defined as

$$\kappa = -(j+\tfrac{1}{2})\,a; \quad a = 1 \quad \text{for} \quad j = l+\tfrac{1}{2}, \quad a = -1 \quad \text{for} \quad j = l-\tfrac{1}{2}. \tag{2.27}$$

The spatial symmetry operations $\hat{\mathrm{H}}_{x,\mathrm{s}}$ and $\hat{\mathrm{H}}_{y,\mathrm{s}}$ transform ϕ_μ to $\pi_\mu - \phi_\mu$ and $-\phi_\mu$ respectively. The operation $\hat{\mathrm{H}}_{z,\mathrm{s}}$ leaves ϕ_μ unchanged but converts θ_μ to $\pi_\mu - \theta_\mu$ if μ is the central atom in an AB_2 molecule, and to $\pi_{B_2} - \theta_{B_2}$ if μ is the first B nucleus (B_1). These transformations taken in conjunction with the results (Brink & Satchler 1962)

$$\begin{aligned} Y_{l,m}(\theta_\mu, \phi_\mu) &= (2\pi)^{-\frac{1}{2}}\, \Theta_{l,m}(\theta_\mu)\, e^{im\phi_\mu}, \\ \Theta_{l,m}(\theta_\mu) &= (-1)^m\, \Theta_{l,-m}(\theta_\mu), \\ \Theta_{l,m}(\pi_\mu - \theta_\mu) &= (-1)^{l-m}\, \Theta_{l,m}(\theta_\mu) \end{aligned}$$

show that

$$\left.\begin{aligned}\hat{\mathrm{H}}_{x,\mathrm{s}}\mathrm{Y}_{l,m}(\theta_\mu,\phi_\mu) &= \mathrm{Y}_{l,-m}(\theta_\mu,\phi_\mu),\\ \hat{\mathrm{H}}_{y,\mathrm{s}}\mathrm{Y}_{l,m}(\theta_\mu,\phi_\mu) &= (-1)^m\mathrm{Y}_{l,-m}(\theta_\mu,\phi_\mu),\\ \hat{\mathrm{H}}_{z,\mathrm{s}}\mathrm{Y}_{l,m}(\theta_\mu,\phi_\mu) &= (-1)^{l-m}\mathrm{Y}_{l,m}(\theta_{\mu'},\phi_{\mu'}),\quad \mu'=\mu,\ \mu=\mathrm{A},\ \mu'=\mathrm{B}_1,\ \mu=\mathrm{B}_2.\end{aligned}\right\}\tag{2.28}$$

It is readily established, by substituting (2.25) into (2.24) and invoking the definitions (2.12) and (2.27) and the symmetry properties of the vector coupling coefficients, that

$$\hat{\mathrm{H}}_{x,\mathrm{t}}|\mathrm{u}_\mu\kappa m\rangle = \mathrm{i}(-1)^{\frac{1}{2}(1-a)}|\mathrm{u}_\mu\kappa-m\rangle,\tag{2.29}$$

$$\hat{\mathrm{H}}_{y,\mathrm{t}}|\mathrm{u}_\mu\kappa m\rangle = (-1)^{m+\frac{1}{2}}(-1)^{\frac{1}{2}(1-a)}|\mathrm{u}_\mu\kappa-m\rangle,\tag{2.30}$$

$$\hat{\mathrm{H}}_{z,\mathrm{t}}|\mathrm{u}_\mu\kappa m\rangle = \mathrm{i}(-1)^{j-m+\frac{1}{2}(1-a)}|\mathrm{u}_{\mu'}\kappa m\rangle,\quad \mu'=\mu,\ \mu=\mathrm{A},\quad \mu'=\mathrm{B}_1,\ \mu=\mathrm{B}_2.\tag{2.31}$$

3. BONDING IN MONOHYDRIDES

(*a*) *The Kappa valence description of monohydrides*

In this and the next section the bonding between a hydrogen atom and a heavy element described in Dirac–Fock theory as consisting of closed subshells (Grant *et al.* 1976) plus a single valence electron occupying a $\bar{\mathrm{p}}$ or p orbital is investigated by using the Kappa valence method. These sections have two main objectives, firstly to extend the previous study of bonding in hydrides and secondly to summarize the methods used throughout this paper to investigate bonding in the Kappa valence approach.

The results (2.29)–(2.31) show that the wavefunction

$$|\psi_{\kappa\mathrm{v}}\rangle = S\hat{\mathscr{A}}[|\mathrm{core}\rangle\tfrac{1}{\sqrt{2}}(|\mathrm{v}\tfrac{1}{2}\rangle|\mathrm{s}-\tfrac{1}{2}\rangle\pm\eta|\mathrm{v}-\tfrac{1}{2}\rangle|\mathrm{s}\tfrac{1}{2}\rangle)],\quad \eta=\pm1,\tag{3.1}$$

is an eigenfunction of $\hat{\mathrm{J}}_{z,\mathrm{T}}$ of zero eigenvalue and of $\hat{\mathrm{H}}_{x,\mathrm{T}}$ and $\hat{\mathrm{H}}_{y,\mathrm{T}}$ with eigenvalue η, and hence that it is an acceptable approximation to $|\psi_\alpha(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)\rangle$. Here $|\mathrm{core}\rangle$ is the Hartree product

$$|\mathrm{core}\rangle = \prod_{i=1}^{N-2}|\mathrm{c}_i(\boldsymbol{r}_i)\rangle\tag{3.2}$$

constructed from the Dirac–Fock core orbitals of the isolated heavy element, $|\mathrm{v}m\rangle$ and $|\mathrm{s}m\rangle$ are the heavy element valence orbitals and hydrogen $|\mathrm{s}\rangle$ orbitals respectively with m denoting the m_j quantum number, S is the normalization integral $\langle\psi_{\kappa\mathrm{v}}|\psi_{\kappa\mathrm{v}}\rangle^{-\frac{1}{2}}$ and $\hat{\mathscr{A}}$ is the antisymmetrizer $(N!)^{-\frac{1}{2}}\Sigma_{\mathrm{P}}(-1)^{\epsilon_{\mathrm{P}}}\hat{\mathrm{P}}$. The positive sign is taken in (3.1) when $|\mathrm{v}\rangle$ is a $\bar{\mathrm{p}}$ orbital, and the negative sign when $|\mathrm{v}\rangle$ is a p orbital. This wavefunction is the Kappa valence wavefunction (Pyper 1980*a*) which, by analogy with the singlet and triplet Heitler–London wavefunctions for the hydrogen molecule, describes the formation of a bond between the hydrogen atom and the heavy element in its *j–j* coupled ground state for $\eta = 1$ and describes repulsion for $\eta = -1$. The calculation used to deduce the bonding properties of a Kappa valence wavefunction consists of four distinct stages which are:

(1) Derive an expression for the total energy ($E_{\kappa\mathrm{v}}$) of the wavefunction as $\langle\psi_{\kappa\mathrm{v}}|\mathscr{H}_{\mathrm{Br}}|\psi_{\kappa\mathrm{v}}\rangle$, using the orthogonality of all the orbitals on any one atom and neglecting both the differential overlap of any core orbital with any orbital belonging to a different atom and differential overlaps of core orbitals on different atoms.

(2) Extract the small (*ca.* 0.2 a.u.) energy of interaction (E_{int}) of the atoms from the large (*ca.* 20000 a.u. for a superheavy element) total energy including internuclear repulsion ($E_{\mathrm{T}\kappa\mathrm{v}}$) by using the atomic Dirac–Fock equations satisfied by the valence orbitals, dropping terms containing the overlaps and differential overlaps neglected in (1). In this approximation the terms $\epsilon_{\mathrm{cv}}\langle sm|\mathrm{c}\rangle$, arising from the off-diagonal Lagrange multipliers present in the atomic Dirac–Fock equations to maintain orbital orthogonality, vanish while the energy of interaction of the nuclei plus the cores becomes $(Z_{\mathrm{E}}-N_{\mathrm{CE}})(Z_{\mathrm{H}}-N_{\mathrm{CH}})/R$. Here Z_{E} and Z_{H} are the charges of the nuclei of the heavy element and the hydrogen atom respectively, N_{CE} and N_{CH} are the respective number of core electrons (for hydrogen $N_{\mathrm{CH}} = 0$) and R is the internuclear distance.

(3) Express E_{int} in terms of purely spatial one- and two-electron integrals, neglecting the small components, which is permissible because E_{int} has no terms linking the large and small components since the Dirac kinetic energy operator ($\mathscr{H}_{\text{k.e.}}$) has been eliminated in step (2).

(4) Compare the form of the expression derived in (3) with those derived from non-relativistic wavefunctions whose bonding characteristics are known.

The general features of this procedure will be illustrated, and results needed throughout this paper will be presented by applying it to the wavefunction (3.1). If the $|\phi_a(\boldsymbol{r})\rangle$ in (2.8) used to construct the projection operators $\mathscr{P}^{(+)}$ entering the Brown hamiltonian ($\mathscr{H}_{\mathrm{Br}}$, (2.1)) are chosen to be Dirac–Fock atomic orbitals of either the isolated heavy element or of the molecule, all the occupied Dirac–Fock atomic orbitals of the isolated atoms can to a good approximation be written as linear combinations of electron-like ($\epsilon_a\rangle - 2c^2$) solutions of (2.8). Hence one has

$$E_{\kappa\mathrm{v}} = \langle\psi_{\kappa\mathrm{v}}|\hat{\mathscr{H}}_{\mathrm{Br}}|\psi_{\kappa\mathrm{v}}\rangle = \langle\psi_{\kappa\mathrm{v}}|\hat{\mathscr{H}}_{\mathrm{T}}|\psi_{\kappa\mathrm{v}}\rangle \tag{3.3a}$$

$$\begin{aligned} &= S^2[\langle\mathrm{core}|\tfrac{1}{\sqrt{2}}(\langle\mathrm{v}\tfrac{1}{2}|\langle\mathrm{s}-\tfrac{1}{2}|\pm\eta\langle\mathrm{v}-\tfrac{1}{2}|\langle\mathrm{s}\tfrac{1}{2}|)]\,\hat{\mathscr{H}}_{\mathrm{T}}\sum_{\mathrm{P}}(-1)^{\epsilon_{\mathrm{P}}}\hat{\mathrm{P}}[|\mathrm{core}\rangle \\ &\quad\times\tfrac{1}{\sqrt{2}}(|\mathrm{v}\tfrac{1}{2}\rangle|\mathrm{s}-\tfrac{1}{2}\rangle\pm\eta|\mathrm{v}-\tfrac{1}{2}\rangle|\mathrm{s}\tfrac{1}{2}\rangle)]. \end{aligned} \tag{3.3b}$$

The energy $E_{\kappa\mathrm{v}}$ required in step (1) is calculated from this equation by using the immediate consequences of (2.29) that if $\hat{\mathrm{O}}(1)$ and $\hat{\mathrm{O}}(1,2)$ are respectively one- and two-electron operators satisfying

$$\left.\begin{aligned} \hat{\mathrm{H}}_{x,\mathrm{t}}^{-1}(1)\,\hat{\mathrm{O}}(1)\,\hat{\mathrm{H}}_{x,\mathrm{t}}(1) &= \hat{\mathrm{O}}(1), \\ \hat{\mathrm{H}}_{x,\mathrm{t}}^{-1}(1)\,\hat{\mathrm{H}}_{x,\mathrm{t}}^{-1}(2)\,\hat{\mathrm{O}}(1,2)\,\hat{\mathrm{H}}_{x,\mathrm{t}}(1)\,\hat{\mathrm{H}}_{x,\mathrm{t}}(2) &= \hat{\mathrm{O}}(1,2) \end{aligned}\right\} \tag{3.4}$$

then

$$\left.\begin{aligned} \langle\mathrm{A}m_{\mathrm{A}}|\hat{\mathrm{O}}|\mathrm{B}m_{\mathrm{B}}\rangle &= (-1)^{\frac{1}{2}(a_{\mathrm{A}}-a_{\mathrm{B}})}\langle\mathrm{A}-m_{\mathrm{A}}|\hat{\mathrm{O}}|\mathrm{B}-m_{\mathrm{B}}\rangle, \\ \langle\mathrm{A}m_{\mathrm{A}}\,\mathrm{C}m_{\mathrm{C}}|\hat{\mathrm{O}}|\mathrm{B}m_{\mathrm{B}}\,\mathrm{D}m_{\mathrm{D}}\rangle &= (-1)^{\frac{1}{2}(a_{\mathrm{A}}+a_{\mathrm{C}}-a_{\mathrm{B}}-a_{\mathrm{D}})}\langle\mathrm{A}-m_{\mathrm{A}}\,\mathrm{C}-m_{\mathrm{C}}|\hat{\mathrm{O}}|\mathrm{B}-m_{\mathrm{B}}\,\mathrm{D}-m_{\mathrm{D}}\rangle, \end{aligned}\right\} \tag{3.5}$$

with $|\mathrm{A}m_{\mathrm{A}}\rangle$, $|\mathrm{B}m_{\mathrm{B}}\rangle$, $|\mathrm{C}m_{\mathrm{C}}\rangle$ and $|\mathrm{D}m_{\mathrm{D}}\rangle$ Dirac–Fock atomic orbitals (2.24). The total energy $E_{\mathrm{T}\kappa\mathrm{v}}$ is found, by explicitly considering each of the permutations in the sum over P in (3.3) and adding the internuclear repulsion, to be

$$\begin{aligned} E_{\mathrm{T}\kappa\mathrm{v}} = S^2[&E_{\mathrm{CE}}+\sum_{\mathrm{c}}\langle\mathrm{c}|\hat{V}_{\mathrm{H}}|\mathrm{c}\rangle+\langle\mathrm{v}\tfrac{1}{2}|\hat{\mathscr{H}}_{\mathrm{D}}+\hat{V}_{\mathrm{DFE}}|\mathrm{v}\tfrac{1}{2}\rangle+\langle\mathrm{s}\tfrac{1}{2}|\hat{\mathscr{H}}_{\mathrm{D}}+\hat{V}_{\mathrm{DFE}}|\mathrm{s}\tfrac{1}{2}\rangle \\ &+2\eta\langle\mathrm{s}\tfrac{1}{2}|\mathrm{v}\tfrac{1}{2}\rangle\langle\mathrm{v}\tfrac{1}{2}|\hat{\mathscr{H}}_{\mathrm{D}}+\hat{V}_{\mathrm{DFE}}|\mathrm{s}\tfrac{1}{2}\rangle+\eta\langle\mathrm{s}\tfrac{1}{2}|\mathrm{v}\tfrac{1}{2}\rangle^2(E_{\mathrm{CE}}+\sum_{\mathrm{c}}\langle\mathrm{c}|\hat{V}_{\mathrm{H}}|\mathrm{c}\rangle) \\ &+\langle\mathrm{v}\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{v}\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}\rangle\pm\eta\langle\mathrm{v}\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{v}-\tfrac{1}{2}\mathrm{s}\tfrac{1}{2}\rangle \\ &\mp\eta\langle\mathrm{v}\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{s}\tfrac{1}{2}\mathrm{v}-\tfrac{1}{2}\rangle-\langle\mathrm{v}\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{s}-\tfrac{1}{2}\mathrm{v}\tfrac{1}{2}\rangle]+Z_{\mathrm{E}}/R, \end{aligned} \tag{3.6a}$$

$$S = (1+\eta\langle\mathrm{v}\tfrac{1}{2}|\mathrm{s}\tfrac{1}{2}\rangle^2)^{-\frac{1}{2}}, \tag{3.6b}$$

where E_{CE} is the energy of the core of the heavy element, $\hat{V}_{\mathrm{H}}$ is the potential due to the proton and $\hat{V}_{\mathrm{DFE}}$ is the Fock operator of the core (equal to $\Sigma_{\mathrm{c}}\hat{\mathrm{J}}_{\mathrm{c}}-\hat{\mathrm{K}}_{\mathrm{c}}$ with $\hat{\mathrm{J}}_{\mathrm{c}}$ and $\hat{\mathrm{K}}_{\mathrm{c}}$ relativistic

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coulomb and exchange operators built from orbital $|c\rangle$). Although the approximations of neglecting overlap between each core orbital and all the orbitals on different centres and multicentre core–core differential overlap may not be quantitatively accurate, they suffice to reveal the qualitative features of the bonding because this arises from the overlap of the valence orbitals. The interaction energy is extracted from (3.6a) (step (2)) by substituting the Dirac–Fock equations satisfied by the valence orbitals,

$$(\hat{\mathscr{H}}_{\text{k.e.}}+\hat{V}_{\text{NE}}+\hat{V}_{\text{DFE}})\,|vm\rangle = \epsilon_{\text{v}}|vm\rangle+\sum_{\text{c}}\epsilon_{\text{cv}}|\text{c}\rangle, \tag{3.7a}$$

$$(\hat{\mathscr{H}}_{\text{k.e.}}+\hat{V}_{\text{H}})\,|sm\rangle = E_{\text{H}}|sm\rangle, \tag{3.7b}$$

with $\hat{V}_{\text{NE}}$ the nuclear potential of the heavy element, into (3.6a) the terms $\epsilon_{\text{cv}}\langle sm|\text{c}\rangle$ being neglected and $\Sigma_{\text{c}}\langle \text{c}|\hat{V}_{\text{H}}|\text{c}\rangle$ being written as $-(Z_{\text{E}}-1)/\text{R}$ in accordance with the approach outlined above. The result is

$$\begin{aligned} E_{\text{T}\kappa\text{v}} &= E_{\text{CE}}+\epsilon_{\text{v}}+E_{\text{H}}+E_{\text{int}} \equiv E_{ats}+E_{\text{int}},\\ E_{\text{int}} &= S^2[\langle \text{v}\tfrac{1}{2}|\hat{V}_{\text{H}}|\text{v}\tfrac{1}{2}\rangle+\langle \text{s}\tfrac{1}{2}|\hat{V}_{\text{NE}}+\hat{V}_{\text{DFE}}|\text{s}\tfrac{1}{2}\rangle+\eta\langle \text{s}\tfrac{1}{2}|\text{v}\tfrac{1}{2}\rangle\langle \text{v}\tfrac{1}{2}|\hat{V}_{\text{NE}}+\hat{V}_{\text{DFE}}+\hat{V}_{\text{H}}|\text{s}\tfrac{1}{2}\rangle\\ &\quad+\langle \text{v}\tfrac{1}{2}\text{s}-\tfrac{1}{2}|r_{12}^{-1}|\text{v}\tfrac{1}{2}\text{s}-\tfrac{1}{2}\rangle\pm\eta\langle \text{v}\tfrac{1}{2}\text{s}-\tfrac{1}{2}|r_{12}^{-1}|\text{v}-\tfrac{1}{2}\text{s}\tfrac{1}{2}\rangle\\ &\quad\mp\eta\langle \text{v}\tfrac{1}{2}\text{s}-\tfrac{1}{2}|r_{12}^{-1}|\text{s}\tfrac{1}{2}\text{v}-\tfrac{1}{2}\rangle-\langle \text{v}\tfrac{1}{2}\text{s}-\tfrac{1}{2}|r_{12}^{-1}|\text{s}-\tfrac{1}{2}\text{v}\tfrac{1}{2}\rangle]+R^{-1}. \end{aligned} \tag{3.8}$$

Since the expression (3.8) contains no operators linking the large and small components, the simultaneous validity of two further results shows that E_{int} can be approximated solely by the terms containing only the large components (step (3)). Firstly, examination of Dirac–Fock calculations for even superheavy elements shows that, for valence orbitals, the ratio $Q(r)/P(r)$ is of order $1/c$ in the outer spatial regions, making the dominant contributions to integrals such as $\langle \text{s}\tfrac{1}{2}|\text{v}\tfrac{1}{2}\rangle$ and $\langle \text{s}\tfrac{1}{2}\text{v}\tfrac{1}{2}|r_{12}^{-1}|\text{v}\tfrac{1}{2}\text{s}\tfrac{1}{2}\rangle$ which are non-zero solely by virtue of the differential overlap of valence orbitals on different centres. Secondly, the results of the atomic Dirac–Fock calculations reported in paper I show that the norms of the large components $1+\text{M}_{\text{v}}/2c^2$ ($\text{M}_{\text{v}} = -c^2\langle \text{v}|1-\beta|\text{v}\rangle$) deviate from unity by approximately 10^{-4} and hence that the errors introduced into direct integrals such as $\langle \text{v}\tfrac{1}{2}\text{s}-\tfrac{1}{2}|r_{12}^{-1}|\text{v}\tfrac{1}{2}\text{s}-\tfrac{1}{2}\rangle$ from loss of normalization will be of the order of 3×10^{-5} a.u. ($\approx$ 7 cm^{-1}) for $R\approx 3$ a.u. which is expected to be typical for a superheavy element (Fricke & Waber 1970). Use of (2.24) and (2.25) shows, the phase conventions of Condon & Shortley (1935) being used, that the large components of Dirac–Fock atomic orbitals, when expressed in terms of the spin functions $|\alpha\rangle$ and $|\beta\rangle$ and spatial orbitals that are eigenfunctions of $\hat{\text{l}}_z$, are

$$\left.\begin{aligned} &|\text{s}\tfrac{1}{2}\rangle_{\text{L}} = |\text{s}_0\,\alpha\rangle,\ |\bar{\text{p}}\tfrac{1}{2}\rangle_{\text{L}} = -\tfrac{1}{\sqrt{3}}|\text{p}_0\,\alpha\rangle+\sqrt{\tfrac{2}{3}}|\text{p}_1\,\beta\rangle,\quad |\text{p}\tfrac{1}{2}\rangle_{\text{L}} = \sqrt{\tfrac{2}{3}}|\text{p}_0\,\alpha\rangle+\tfrac{1}{\sqrt{3}}|\text{p}_1\,\beta\rangle,\\ &|\text{s}-\tfrac{1}{2}\rangle_{\text{L}} = |\text{s}_0\,\beta\rangle,\ |\bar{\text{p}}-\tfrac{1}{2}\rangle_{\text{L}} = \tfrac{1}{\sqrt{3}}|\text{p}_0\,\beta\rangle-\sqrt{\tfrac{2}{3}}|\text{p}_{-1}\,\alpha\rangle,\quad |\text{p}-\tfrac{1}{2}\rangle_{\text{L}} = \sqrt{\tfrac{2}{3}}|\text{p}_0\,\beta\rangle+\tfrac{1}{\sqrt{3}}|\text{p}_{-1}\,\alpha\rangle,\\ &\qquad\qquad |\text{p}\,\tfrac{3}{2}\rangle_{\text{L}} = |\text{p}_1\,\alpha\rangle,\quad |\text{p}-\tfrac{3}{2}\rangle_{\text{L}} = |\text{p}_{-1}\,\beta\rangle, \end{aligned}\right\} \tag{3.9}$$

where the numerical subscripts denote the $\hat{\text{l}}_z$ eigenvalues, and subscript L denotes the large components. Substitution of these results in (3.8) converts this to

$$\begin{aligned} E_{\text{int}} &= aS^2[\langle \text{p}_0|\hat{V}_{\text{H}}|\text{p}_0\rangle+\langle \text{s}_0|\hat{V}_{\text{E}}|\text{s}_0\rangle+\eta\langle \text{s}_0|\text{p}_0\rangle\langle \text{p}_0|\hat{V}_{\text{E}}+\hat{V}_{\text{H}}|\text{s}_0\rangle\\ &\quad+\langle \text{p}_0\text{s}_0|r_{12}^{-1}|\text{p}_0\text{s}_0\rangle+\eta\langle \text{p}_0\text{s}_0|r_{12}^{-1}|\text{s}_0\text{p}_0\rangle+(1+\eta\langle \text{s}_0|\text{p}_0\rangle^2)\,R^{-1}]\\ &\quad+(1-a)\,S^2[\langle \text{p}_1|\hat{V}_{\text{H}}|\text{p}_1\rangle+\langle \text{s}_0|\hat{V}_{\text{E}}|\text{s}_0\rangle+\langle \text{p}_1\text{s}_0|r_{12}^{-1}|\text{p}_1\text{s}_0\rangle\\ &\quad-\langle \text{p}_1\text{s}_0|r_{12}^{-1}|\text{s}_0\text{p}_1\rangle+R^{-1}], \end{aligned} \tag{3.10a}$$

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$$S = (1 + a\eta\langle \mathrm{s}_0|\mathrm{p}_0\rangle^2)^{-\frac{1}{2}}, \tag{3.10b}$$

$$\hat{V}_{\mathrm{E}} = \hat{V}_{\mathrm{NE}} + \hat{V}'_{\mathrm{DFE}}, \tag{3.10c}$$

$$\begin{aligned}\langle \mathrm{d}|\hat{V}'_{\mathrm{DFE}}|\mathrm{e}\rangle &= \langle \mathrm{d}\alpha|\hat{V}'_{\mathrm{DFE}}|\mathrm{d}\alpha\rangle = \langle \mathrm{d}\beta|\hat{V}'_{\mathrm{DFE}}|\mathrm{d}\beta\rangle \\ &= \sum_{\mathrm{c}} \left\langle \mathrm{d}(r_1)\left|\int \mathrm{c}^{+}(r_2)\, r_{12}^{-1}\, \mathrm{c}(r_2)\,\mathrm{d}r_2\right|\mathrm{e}(r_1)\right\rangle - \langle \mathrm{d}\alpha\mathrm{c}^{\mathrm{L}}|r_{12}^{-1}|\mathrm{c}^{\mathrm{L}}\mathrm{e}\alpha\rangle. \end{aligned} \tag{3.10d}$$

Here $\hat{V}'_{\mathrm{DFE}}$ differs from $\hat{V}_{\mathrm{DFE}}$ solely by the omission of terms in the exchange operators containing small components, (3.10*d*) defining its matrix elements between the spinless one-component functions $|\mathrm{d}\rangle$ and $|\mathrm{e}\rangle$. The quantity a in (3.10*a*) is $\frac{1}{3}$ when $|vm\rangle$ is a $\bar{\mathrm{p}}$ orbital while it is $\frac{2}{3}$ if $|vm\rangle$ is a p orbital.

The result (3.10*a*) is interpreted (step (4)) by introducing the non-relativistic wavefunctions

$$|^{1,3}\Sigma\rangle = (1+\eta^{\mathrm{NR}}\langle \mathrm{s}^{\mathrm{NR}}|\mathrm{p}^{\mathrm{NR}}\rangle^2)^{-\frac{1}{2}}\, \hat{\mathscr{A}}[|\mathrm{core}^{\mathrm{NR}}\rangle|\mathrm{p}_0^{\mathrm{NR}}\rangle|\mathrm{s}^{\mathrm{NR}}\rangle\, \tfrac{1}{\sqrt{2}}|\alpha\beta - \eta^{\mathrm{NR}}\beta\alpha\rangle], \tag{3.11a}$$

$$|^{3,1}\Pi\rangle = \hat{\mathscr{A}}[|\mathrm{core}^{\mathrm{NR}}\rangle|\mathrm{p}_1^{\mathrm{NR}}\rangle|\mathrm{s}^{\mathrm{NR}}\rangle\, \tfrac{1}{\sqrt{2}}|\alpha\beta + \eta^{\mathrm{NR}}\beta\alpha\rangle], \tag{3.11b}$$

where $\eta^{\mathrm{NR}} = 1$ for the $|^1\Sigma\rangle$ and $|^3\Pi\rangle$ functions but $\eta^{\mathrm{NR}} = -1$ for the $|^3\Sigma\rangle$ and $|^1\Pi\rangle$ ones. The orbitals $|\mathrm{p}_m^{\mathrm{NR}}\rangle$ and $|\mathrm{s}^{\mathrm{NR}}\rangle$ are spatial one-component non-relativistic Hartree–Fock atomic orbitals satisfying the non-relativistic analogues of (3.7). Methods identical to those used to derive (3.10), except that $\hat{\mathscr{H}}_{\mathrm{Br}}$ is replaced by the Schrödinger hamiltonian, show that

$$\begin{aligned} E_{\mathrm{int}}(^{1,3}\Sigma) = {} & (1+\eta^{\mathrm{NR}}\langle \mathrm{s}^{\mathrm{NR}}|\mathrm{p}_0^{\mathrm{NR}}\rangle^2)^{-1}(\langle \mathrm{p}_0^{\mathrm{NR}}|\hat{V}_{\mathrm{H}}|\mathrm{p}_0^{\mathrm{NR}}\rangle + \langle \mathrm{s}^{\mathrm{NR}}|\hat{V}_{\mathrm{E}}^{\mathrm{NR}}|\mathrm{s}^{\mathrm{NR}}\rangle \\ & + \eta\langle \mathrm{s}^{\mathrm{NR}}|\mathrm{p}_0^{\mathrm{NR}}\rangle\langle \mathrm{p}_0^{\mathrm{NR}}|\hat{V}_{\mathrm{E}}^{\mathrm{NR}} + \hat{V}_{\mathrm{H}}|\mathrm{s}^{\mathrm{NR}}\rangle + \langle \mathrm{p}_0^{\mathrm{NR}}\mathrm{s}^{\mathrm{NR}}|r_{12}^{-1}|\mathrm{p}_0^{\mathrm{NR}}\mathrm{s}^{\mathrm{NR}}\rangle \\ & + \eta\langle \mathrm{p}_0^{\mathrm{NR}}\mathrm{s}^{\mathrm{NR}}|r_{12}^{-1}|\mathrm{s}^{\mathrm{NR}}\mathrm{p}_0^{\mathrm{NR}}\rangle) + R^{-1}, \end{aligned} \tag{3.12a}$$

$$\begin{aligned} E_{\mathrm{int}}(^{3,1}\Pi) = {} & \langle \mathrm{p}_1^{\mathrm{NR}}|\hat{V}_{\mathrm{H}}|\mathrm{p}_1^{\mathrm{NR}}\rangle + \langle \mathrm{s}^{\mathrm{NR}}|\hat{V}_{\mathrm{E}}^{\mathrm{NR}}|\mathrm{s}^{\mathrm{NR}}\rangle + \langle \mathrm{p}_1^{\mathrm{NR}}\mathrm{s}^{\mathrm{NR}}|r_{12}^{-1}|\mathrm{p}_1^{\mathrm{NR}}\mathrm{s}^{\mathrm{NR}}\rangle \\ & - \eta\langle \mathrm{p}_1^{\mathrm{NR}}\mathrm{s}^{\mathrm{NR}}|r_{12}^{-1}|\mathrm{s}^{\mathrm{NR}}\mathrm{p}_1^{\mathrm{NR}}\rangle + R^{-1}. \end{aligned} \tag{3.12b}$$

The function $|^1\Sigma\rangle$ with interaction energy $E_{\mathrm{int}}(^1\Sigma)$ is readily interpreted since it is a Heitler–London non-orthogonal singlet wavefunction describing the formation of a normal covalent bond. The interpretation of the function $|^3\Pi\rangle$, which describes the interaction of two atoms each containing one valence electron whose spins are parallel and which occupy orthogonal orbitals, is not standard because experimental examples of such systems seem to be rare. The case of Si_2 (and O_2) differs from that of the wavefunction (3.11*b*) because the methods used to derive (3.12) show that the interaction energy predicted by the valence bond wavefunction $\hat{\mathscr{A}}[|\mathrm{sigma}\rangle\, \frac{1}{\sqrt{2}}(\mathrm{p}_{1,\mathrm{A}}\mathrm{p}_{-1,\mathrm{B}} - \mathrm{p}_{-1,\mathrm{A}}\mathrm{p}_{1,\mathrm{B}})\, \frac{1}{\sqrt{2}}|\alpha\beta - \beta\alpha\rangle]$ ($|\mathrm{sigma}\rangle$ is the portion of wavefunction built from σ orbitals) for the $^3\Sigma_{\mathrm{g}}^{-}$ ground state of Si_2 contains terms of the type $\langle \mathrm{p}_{1,\mathrm{A}}|\mathrm{p}_{1,\mathrm{B}}\rangle \langle \mathrm{p}_{1,\mathrm{B}}|\hat{V}_{\mathrm{A}} + \hat{V}_{\mathrm{B}}|\mathrm{p}_{1,\mathrm{A}}\rangle$ ($\hat{V}_{\mathrm{A}}$ and $\hat{V}_{\mathrm{B}}$ are the potentials entering the atomic Fock operators) which characterize the non-orthogonal Heitler–London singlet interaction energy (3.12*a*). It has been pointed out (Pyper 1980*a*) that the lowest $^3\Pi$ excited states of the group IIIB hydrides do not provide experimental examples of orthogonal triplet bonds because for BH the minimum in the potential energy curve for this state arises from an avoided curve crossing. It has been subsequently pointed out (Pitzer & Christiansen 1981) that the minima in the potential energy curves for the lowest $^3\Pi$ states of GaH and InH similarly arise from avoided crossings. Furthermore the model pseudopotential calculations on TlH (Pitzer & Christiansen 1981) confirmed the fact already known and discussed for BH (Pyper 1980*a*) that due to the overlap of the hydrogen ls orbital with the closed valence s^2 subshell the bonding between a hydrogen atom and the s^2p_π configuration of a group IIIB element is small or even non-existent. In the light of these data showing that the $^3\Pi$ states of the known group IIIB hydrides cannot serve as models of an orthogonal triplet bond, the calculations of TlH cannot be construed as evidence that the present theory (Pyper 1980*a* and below), which assumes that the core orbitals $|c_i\rangle$, (3.2), play no role in the bonding, is incorrect. The outermost s orbital of the known group IIIB elements is too expanded and loosely bound to be regarded as a core orbital. Furthermore it should be pointed out that the high ionicity of TlH is yet a further reason why calculations on this system do not test the description of purely covalent bonds presented in this section because it is shown below (§3(*b*)) that bonds containing substantial quantities of both covalent and ionic characters are affected by further factors.

On the basis of the experimental dissociation energies of the $^3\Pi_r$ excited states of CuH and AgH, which do not seem to have the features rendering the group IIIB hydrides unsuitable models, it was suggested (Pyper 1980*a*) that the order of an orthogonal triplet bond is $\frac{1}{2}$. Furthermore the non-relativistic molecular orbital description of these states by the configuration $(n-1)\,d^{10}\sigma^1 np^1_\pi$, where σ is the fully bonding orbital $s(ns+1s_H)/\surd 2$ undoubtedly predicts a bond order of $\frac{1}{2}$ without any assumptions being made beyond those standard in molecular orbital theory. This suggests, based on the evidence currently available, that the bond described by the function $|^3\Pi\rangle$ (3.11*a*) should be taken to have an order of $\frac{1}{2}$.

Comparison of the expressions (3.12) for the interaction energies of the functions (3.11) with the interaction energy (3.10) shows, with the order of the bond described by the function $|^3\Pi\rangle$ taken to be $\frac{1}{2}$ as discussed above, that the orders of the purely covalent bonds described by the totally symmetric wave functions (3.1) having $\eta = 1$ are $S^2[\frac{1}{2}(1+a)+a\langle s_0|p_0\rangle^2]$. These orders become $\frac{2}{3}$ and $\frac{5}{6}$ for $\bar{p}$–H and p–H bonds respectively in the limit that $a\langle s_0|p_0\rangle^2$ is small. Comparison of (3.10*a*) for $\eta = -1$ with $E_{\text{int}}(^3\Sigma)$ and $E_{\text{int}}(^3\Pi)$ shows that the non-totally-symmetric wavefunctions (3.1) having $\eta = -1$ consist of a mixture of a strongly repulsive Heitler–London non-orthogonal triplet wavefunction and a weakly bonding (bond order $\frac{1}{2}$) orthogonal triplet function ((3.11*b*) with $\eta^{\text{NR}} = 1$).

(*b*) *The role of ionic–covalent resonance*

The results that the orders of $\bar{p}$–H and p–H bonds are $\frac{2}{3}$ and $\frac{5}{6}$ respectively in the small-overlap limit suggest that, although the large $\bar{p} \rightarrow p$ excitation energies in heavy elements greatly inhibit bonding described by the relativistic valence bond method, the overall effect of relativity is not to inhibit the formation of purely covalent bonds. However, it is well known that a covalent bond between a pair of elements A and B of significantly different electronegativity has larger bond energy (D_{AB}) than the average ($\frac{1}{2}(D_{AA}+D_{BB})$) of the bond energies of the A–A and B–B bonds if the A–B bond is formed from a hard Lewis acid, hard Lewis base pair (Pearson 1968*a*, *b*). The assumption made in the following treatment that the core of the heavy element does not actively participate in the bonding implies that the ion E^+ is a hard Lewis acid (Pearson 1968*a*, *b*). Such an increased bond energy can be naturally explained by non-relativistic valence bond theory as the energy lowering occurring when wavefunctions describing the ionic systems A^-B^+ and A^+B^- are added to a covalent Heitler–London wavefunction of the type $|^1\Sigma\rangle$ (Pauling 1932), which mechanism is known as ionic–covalent resonance. The possibility and extent of resonance stabilization of Kappa valence wavefunctions must be examined if the chemistry of heavy elements is to be fully understood.

The heavy elements of groups IIIB and VB of the Periodic Table, which are those having a single $\bar{\mathrm{p}}$ or p electron outside closed subshells, are less electronegative than hydrogen. Hence only resonance between the function (3.1) and the ionic structure (denoted $|\psi_{\mathrm{ion}}\rangle$) $\mathrm{E^+H^-}$ will be investigated in detail. Application of the four-step process described above requires both that the ionic function be constructed from the orbitals satisfying (3.7) used in (3.1) and that both relativistic and non-relativistic wavefunctions be considered. These wavefunctions are

$$|\psi_{\mathrm{res}}\rangle = c_1|\psi_{\kappa\mathrm{v}}\rangle + c_2|\psi_{\mathrm{ion}}\rangle, \tag{3.13}$$

and

$$|\psi_{\mathrm{res}}^{\mathrm{NR}}\rangle = c_1^{\mathrm{NR}}|{}^1\Sigma\rangle + c_2^{\mathrm{NR}}|\psi_{\mathrm{ion}}^{\mathrm{NR}}\rangle \tag{3.14}$$

with

$$\langle\psi_{\mathrm{res}}|\psi_{\mathrm{res}}\rangle = \langle\psi_{\mathrm{res}}^{\mathrm{NR}}|\psi_{\mathrm{res}}^{\mathrm{NR}}\rangle = 1, \tag{3.15}$$

where the coefficients c_i and c_i^{NR} are determined as usual by solving the secular equations $|H-E\Delta| = 0$, and the ionic wavefunctions are

$$|\psi_{\mathrm{ion}}\rangle = \hat{\mathscr{A}}[|\mathrm{core}\rangle|\mathrm{s}\tfrac{1}{2}\rangle|\mathrm{s}-\tfrac{1}{2}\rangle], \tag{3.16}$$

$$|\psi_{\mathrm{ion}}^{\mathrm{NR}}\rangle = \hat{\mathscr{A}}[|\mathrm{core}^{\mathrm{NR}}\rangle|\mathrm{s}^{\mathrm{NR}}\alpha\rangle|\mathrm{s}^{\mathrm{NR}}\beta\rangle]. \tag{3.17}$$

In (3.13) $|\psi_{\kappa\mathrm{v}}\rangle$ is the totally symmetric wavefunction (3.1) having $\eta = 1$ while the results (2.29)–(2.31) show that the ionic function $|\psi_{\mathrm{ion}}\rangle$ has the same symmetry as $|\psi_{\kappa\mathrm{v}}\rangle$, being an eigenfunction of $\hat{\mathrm{J}}_{z,\mathrm{T}}$, $\hat{\mathrm{H}}_{x,\mathrm{T}}$ and $\hat{\mathrm{H}}_{y,\mathrm{T}}$ with eigenvalues 0, 1 and 1 respectively. The elements of hamiltonian and overlap matrices entering the secular equations determining the energy and coefficients c_1 and c_2 are found, with overlap between the core orbitals $|c\rangle$ and the hydrogen orbitals being neglected, to be

$$\begin{aligned}
H_{22} &= \langle\psi_{\mathrm{ion}}|\hat{\mathscr{H}}_{\mathrm{Br}} + Z_{\mathrm{E}}/R|\psi_{\mathrm{ion}}\rangle = E_{\mathrm{CE}} + 2E_{\mathrm{H}} + 2\langle \mathrm{s}\tfrac{1}{2}|\hat{V}_{\mathrm{NE}} + \hat{V}_{\mathrm{DFE}}|\mathrm{s}\tfrac{1}{2}\rangle \\
&\quad + \langle \mathrm{s}\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{s}\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}\rangle - \langle \mathrm{s}\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{s}-\tfrac{1}{2}\mathrm{s}\tfrac{1}{2}\rangle + R^{-1} \\
&\equiv E_{\mathrm{ats}} + E_{\mathrm{H}} - \epsilon_{\mathrm{v}} + 2\langle \mathrm{s}\tfrac{1}{2}|\hat{V}_{\mathrm{NE}} + \hat{V}_{\mathrm{DFE}}|\mathrm{s}\tfrac{1}{2}\rangle + \langle \mathrm{s}\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{s}\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}\rangle \\
&\quad - \langle \mathrm{s}\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{s}-\tfrac{1}{2}\mathrm{s}\tfrac{1}{2}\rangle + R^{-1} \\
&\equiv E_{\mathrm{ats}} + E_{\mathrm{int}}(\psi_{\mathrm{ion}}),
\end{aligned} \tag{3.18}$$

$$\begin{aligned}
H_{21} &= \langle\psi_{\mathrm{ion}}|\hat{\mathscr{H}}_{\mathrm{Br}} + Z_{\mathrm{E}}/R|\psi_{\kappa\mathrm{v}}\rangle = \surd 2S[\langle \mathrm{s}\tfrac{1}{2}|\mathrm{v}\tfrac{1}{2}\rangle(E_{\mathrm{CE}} + R^{-1} + \langle \mathrm{s}\tfrac{1}{2}|\hat{\mathscr{H}}_{\mathrm{k.e.}} + \hat{V}_{\mathrm{H}} + \hat{V}_{\mathrm{NE}} + \hat{V}_{\mathrm{DFE}}|\mathrm{s}\tfrac{1}{2}\rangle) \\
&\quad + \langle \mathrm{s}\tfrac{1}{2}|\hat{\mathscr{H}}_{\mathrm{k.e.}} + \hat{V}_{\mathrm{H}} + \hat{V}_{\mathrm{NE}} + \hat{V}_{\mathrm{DFE}}|\mathrm{v}\tfrac{1}{2}\rangle + \langle \mathrm{s}\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{v}\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}\rangle - \langle \mathrm{s}\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{s}-\tfrac{1}{2}\mathrm{v}\tfrac{1}{2}\rangle] \\
&= \surd 2S\langle \mathrm{s}\tfrac{1}{2}|\mathrm{v}\tfrac{1}{2}\rangle(E_{\mathrm{CE}} + E_{\mathrm{H}} + \epsilon_{\mathrm{v}}) + \surd 2\,S[\langle \mathrm{s}\tfrac{1}{2}|\mathrm{v}\tfrac{1}{2}\rangle(\langle \mathrm{s}\tfrac{1}{2}|\hat{V}_{\mathrm{NE}} + \hat{V}_{\mathrm{DFE}}|\mathrm{s}\tfrac{1}{2}\rangle + R^{-1}) \\
&\quad + \langle \mathrm{s}\tfrac{1}{2}|\hat{V}_{\mathrm{H}}|\mathrm{v}\tfrac{1}{2}\rangle + \langle \mathrm{s}\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{v}\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}\rangle - \langle \mathrm{s}\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{s}-\tfrac{1}{2}\mathrm{v}\tfrac{1}{2}\rangle] \\
&\equiv \surd 2\,S\langle \mathrm{s}\tfrac{1}{2}|\mathrm{v}\tfrac{1}{2}\rangle E_{\mathrm{ats}} + E_{\mathrm{int}}(\mathrm{i}-\kappa\mathrm{v}),
\end{aligned} \tag{3.19}$$

$$\Delta_{22} = \langle\psi_{\mathrm{ion}}|\psi_{\mathrm{ion}}\rangle = 1, \tag{3.20}$$

$$\Delta_{21} = \langle\psi_{\mathrm{ion}}|\psi_{\kappa\mathrm{v}}\rangle = \surd 2\,S\langle \mathrm{s}\tfrac{1}{2}|\mathrm{v}\tfrac{1}{2}\rangle, \tag{3.21}$$

where the equations (3.7) were used in the second step in (3.19). The element $\langle\psi_{\kappa\mathrm{v}}|(\hat{\mathscr{H}}_{\mathrm{Br}} + Z_{\mathrm{E}}/R)|\psi_{\kappa\mathrm{v}}\rangle$ has already been calculated, (3.8), while $\Delta_{11} = 1$.

The change in the resonance stabilization energy on passing from the non-relativistic function (3.14) to the relativistic one (3.13) arises both from differences between the mixing coefficients c_i and c_i^{NR} and from the difference between $E_{\mathrm{int}}(\mathrm{i}-\kappa\mathrm{v})$ and its non-relativistic analogue $E_{\mathrm{int}}^{\mathrm{NR}}(\mathrm{i}-{}^1\Sigma)$. However, the origin of the change in resonance energy is revealed by examining $E_{\mathrm{int}}(\mathrm{i}-\kappa\mathrm{v})$ and $E_{\mathrm{int}}^{\mathrm{NR}}(\mathrm{i}-{}^1\Sigma)$ because the change in the coefficients is caused by that in the matrix elements. The relations (3.9) show that $E_{\mathrm{int}}(\mathrm{i}-\kappa\mathrm{v})$ and $E^{\mathrm{NR}}_{\mathrm{int}}(\mathrm{i}-{}^1\Sigma)$, when approximated solely by the large components, become

$$E_{\mathrm{int}}(\mathrm{i}-\kappa\mathrm{v}) = \mp(2a)^{\frac{1}{2}} H_{\mathrm{int}}/(1+a\langle \mathrm{s}_0|\mathrm{p}_0\rangle^2)^{\frac{1}{2}}, \tag{3.22a}$$

$$H_{\mathrm{int}} = \langle \mathrm{s}_0|\mathrm{p}_0\rangle\langle \mathrm{s}_0|\hat{V}_{\mathrm{E}}+1/R|\mathrm{s}_0\rangle+\langle \mathrm{s}_0|\hat{V}_{\mathrm{H}}|\mathrm{p}_0\rangle+\langle \mathrm{s}_0\mathrm{s}_0|r_{12}^{-1}|\mathrm{s}_0\mathrm{p}_0\rangle, \tag{3.22b}$$

$$E^{\mathrm{NR}}_{\mathrm{int}}(\mathrm{i}-{}^1\Sigma) = \sqrt{2}\, H^{\mathrm{NR}}_{\mathrm{int}}/(1+\langle \mathrm{s}^{\mathrm{NR}}|\mathrm{p}_0^{\mathrm{NR}}\rangle^2)^{\frac{1}{2}}, \tag{3.23a}$$

$$H^{\mathrm{NR}}_{\mathrm{int}} = \langle \mathrm{s}^{\mathrm{NR}}|\mathrm{p}_0^{\mathrm{NR}}\rangle\langle \mathrm{s}^{\mathrm{NR}}|\hat{V}^{\mathrm{NR}}_{\mathrm{E}}+1/R|\mathrm{s}^{\mathrm{NR}}\rangle+\langle \mathrm{s}^{\mathrm{NR}}|\hat{V}_{\mathrm{H}}|\mathrm{p}_0^{\mathrm{NR}}\rangle+\langle \mathrm{s}^{\mathrm{NR}}\mathrm{s}^{\mathrm{NR}}|r_{12}^{-1}|\mathrm{s}^{\mathrm{NR}}\mathrm{p}_0^{\mathrm{NR}}\rangle, \tag{3.23b}$$

where the negative sign is taken for the $\bar{\mathrm{p}}$ case and the positive sign for the p one. Although neither the two relativistic expressions (3.22*a*, *b*) (both $\bar{\mathrm{p}}$ and p valence orbitals must be considered) nor the expression (3.23*a*) for $E^{\mathrm{NR}}_{\mathrm{int}}(\mathrm{i}-{}^1\Sigma)$ have the same denominators, it is readily seen that the differences between these three will be dominated by changes in the coefficient a (for $\bar{\mathrm{p}}$, $a = \frac{1}{3}$; for p $a = \frac{2}{3}$; while $a = 1$ for $E^{\mathrm{NR}}_{\mathrm{int}}(\mathrm{i}-{}^1\Sigma)$) even for values of the overlap $|\langle \mathrm{s}_0|\mathrm{p}_0\rangle|$ as large as $\frac{1}{3}$. This shows that the resonance stabilization of covalent bonds between a hydrogen atom and a heavy element in its *j–j* coupled ground state is considerably reduced compared with that possible in the relativistic valence bond method and that this reduction is greater for $\bar{\mathrm{p}}$–H bonds than for p–H ones. These results are readily understood by recognizing that the overall symmetry of the upper components of the multi-electron wavefunction $|\psi_{\mathrm{ion}}\rangle$ is ${}^1\Sigma$ while the upper components of the functions (3.1) can be expressed as a sum of two terms, one of ${}^1\Sigma$ symmetry and one of ${}^3\Pi$ symmetry. The ${}^3\Pi$ symmetry term cannot contribute to $E_{\mathrm{int}}(\mathrm{i}-\kappa\mathrm{v})$ because the matrix elements $\langle {}^3\Pi|\hat{V}_{\mathrm{nuc}}+\hat{V}_{\mathrm{el}}|{}^1\Sigma\rangle$ vanish while the ${}^1\Sigma$ symmetry portion of the upper components is less in a $\bar{\mathrm{p}}$–H bond than in a p–H one.

The magnitudes of the ionic–covalent resonance contributions to the binding energies predicted by using the wavefunctions (3.13) and (3.14) are calculated by solving the secular equations. This is most conveniently achieved by introducing the normalized function $(1-|\langle\psi_{\mathrm{ion}}|\psi_{\kappa\mathrm{v}}\rangle|^2)^{-\frac{1}{2}}(|\psi_{\mathrm{ion}}\rangle-\langle\psi_{\kappa\mathrm{v}}|\psi_{\mathrm{ion}}\rangle|\psi_{\kappa\mathrm{v}}\rangle)$ and its non-relativistic analogue, and then diagonalizing the matrix arising from $|\psi_{\kappa\mathrm{v}}\rangle$ and this function. This matrix when expressed in terms of the elements of H given by (3.8), (3.18) and (3.19) becomes, with the use of the notation $\varDelta_{12} \equiv \varDelta$,

$$\begin{bmatrix} H_{11} & (H_{12}-\varDelta H_{11})(1-|\varDelta|^2)^{-\frac{1}{2}} \\ (H_{21}-\varDelta^* H_{11})(1-|\varDelta|^2)^{-\frac{1}{2}} & (H_{22}+|\varDelta|^2H_{11}-\varDelta H_{12}-\varDelta^*H_{21})(1-|\varDelta|^2)^{-1} \end{bmatrix} \tag{3.24}$$

$$\equiv E_{\mathrm{ats}} + \begin{bmatrix} E_{\mathrm{int}} & [E_{\mathrm{int}}(\mathrm{i}-\kappa\mathrm{v})^*-\varDelta E_{\mathrm{int}}](1-|\varDelta|^2)^{-1} \\ [E_{\mathrm{int}}(\mathrm{i}-\kappa\mathrm{v})-\varDelta^* E_{\mathrm{int}}](1-|\varDelta|^2)^{-\frac{1}{2}} & \begin{array}{r}[E_{\mathrm{int}}(\psi_{\mathrm{ion}})+|\varDelta|^2E_{\mathrm{int}}-\varDelta E_{\mathrm{int}}(\mathrm{i}-\kappa\mathrm{v}) \\ -\varDelta^*E_{\mathrm{int}}(\mathrm{i}-\kappa\mathrm{v})](1-|\varDelta|^2)^{-1}\end{array} \end{bmatrix}$$

$$\equiv E_{\mathrm{ats}} + \begin{bmatrix} E_{\mathrm{int}} & H^{\mathrm{or}}_{12} \\ H^{\mathrm{or}}_{21} & H^{\mathrm{or}}_{22} \end{bmatrix}. \tag{3.25}$$

It is shown in Appendix 3 both by considering the simplest ionic model for bonding of superheavy elements and by examining intermediate results of valence bond calculations that there is good evidence for believing that $H^{\mathrm{or}}_{22}-E_{\mathrm{int}}$ is greater than $|H^{\mathrm{or}}_{12}|$. The qualitative features of the bonding can be elucidated by expanding the energy E_{res} of $|\psi_{\mathrm{res}}\rangle$ obtained as the lowest root of (3.25) and retaining only the leading term

$$E_{\mathrm{res}} = E_{\mathrm{ats}}+\tfrac{1}{2}(E_{\mathrm{int}}+H^{\mathrm{or}}_{22})-\tfrac{1}{2}(H^{\mathrm{or}}_{22}-E_{\mathrm{int}})[1+4(H^{\mathrm{or}}_{12})^2/(H^{\mathrm{or}}_{22}-E_{\mathrm{int}})^2]^{\frac{1}{2}}, \tag{3.26a}$$

$$E_{\mathrm{res}} \approx E_{\mathrm{ats}}+E_{\mathrm{int}}-[E_{\mathrm{int}}(\mathrm{i}-\kappa\mathrm{v})-\varDelta E_{\mathrm{int}}]^2/[E_{\mathrm{int}}(\psi_{\mathrm{ion}})-E_{\mathrm{int}}-2\varDelta(E_{\mathrm{int}}(\mathrm{i}-\kappa\mathrm{v})-\varDelta E_{\mathrm{int}})]. \tag{3.26b}$$

Examination of the matrix (3.25) not only confirms that $E_{\text{int}}(\mathrm{i}-\kappa\mathrm{v})$ is primarily responsible for the resonance stabilization, but also pinpoints the mechanism more precisely because the additional term $-\varDelta E_{\text{int}}$ in H_{12}^{or} is the correction to the purely molecular part of the matrix element $\langle\psi_{\text{ion}}|\hat{\mathscr{H}}_{\text{Br}}+Z_{\text{E}}/R)\,|\psi_{\kappa\text{v}}\rangle$ which arises solely because $|\psi_{\kappa\text{v}}\rangle$ and $|\psi_{\text{ion}}\rangle$ are not orthogonal. The approximate form of E_{res}, (3.26*b*), showing that the entire resonance stabilization is proportional to $(H_{12}^{\text{or}})^2$ underlines the significance of this term.

The explicit expressions for H_{12}^{or} and its non-relativistic analogue are found from (3.22) and (3.23), when expressed solely in terms of the large components, to be

$$H_{12}^{\text{or}} = \mp\sqrt{2a}(H_{\text{int}}-\langle \mathrm{s}_0|\mathrm{p}_0\rangle E_{\text{int}})/(1+a\langle \mathrm{s}_0|\mathrm{p}_0\rangle^2)^{\frac{1}{2}}, \tag{3.27a}$$

$$H_{12}^{\text{or NR}} = \sqrt{2}[H_{\text{int}}^{\text{NR}}-\langle \mathrm{s}^{\text{NR}}|\mathrm{p}^{\text{NR}}\rangle E_{\text{int}}(^1\Sigma)]/(1+\langle \mathrm{s}^{\text{NR}}|\mathrm{p}_0^{\text{NR}}\rangle^2)^{\frac{1}{2}}. \tag{3.27b}$$

Since the term $\varDelta(E_{\text{int}}(\mathrm{i}-\kappa\mathrm{v})-\varDelta E_{\text{int}})$ in the denominator in (3.26*b*) will be much smaller than $|E_{\text{int}}(\psi_{\text{ion}})-E_{\text{int}}|$, and the latter quantity will not change significantly when the two relativistic and the non-relativistic cases are compared, it follows that the differences in the resonance contributions to the bonding for the three systems will be dominated by changes in (3.27). Furthermore these changes will arise mainly from changes in the $\sqrt{a}(1+a\langle \mathrm{s}_0|\mathrm{p}_0\rangle^2)^{\frac{1}{2}}$-factor not only because the purely covalent bond energies E_{int} will not differ greatly because $\bar{\mathrm{p}}$–H, p–H and p^{NR}–H bonds have been shown to have orders of $\frac{2}{3}$, $\frac{5}{6}$ and 1 respectively but also because E_{int} is multiplied by the overlap $\langle \mathrm{s}_0|\mathrm{p}_0\rangle$. This shows that the resonance stabilization energies of $\bar{\mathrm{p}}$–H and p–H bonds are smaller by factors of $\frac{1}{3}(1+\langle \mathrm{s}_0|\mathrm{p}_0\rangle^2)/(1+\frac{1}{3}\langle \mathrm{s}_0|\mathrm{p}_0\rangle^2)$ and $\frac{2}{3}(1+\langle \mathrm{s}_0|\mathrm{p}_0\rangle^2)/(1+\frac{2}{3}\langle \mathrm{s}_0|\mathrm{p}_0\rangle^2)$ respectively than that of a corresponding non-relativistic bond. Each of these fractions is identical to the fraction of the Heitler–London non-relativistic energy, entering the purely covalent bond energy E_{int}, (3.10*a*), arising from the Heitler–London singlet portion of the upper components of $|\psi_{\kappa\text{v}}\rangle$. This result coupled with the previous observation that only this singlet portion contributes to the term $E_{\text{int}}(\mathrm{i}-\kappa\mathrm{v})$ primarily responsible for the resonance stabilization shows that in the approximation (3.26) only the Heitler–London singlet contribution to the bonding between a hydrogen atom and a heavy element in its *j–j* coupled ground state can be stabilized by ionic–covalent resonance. These fractions depend only weakly on the overlap $\langle \mathrm{s}_0|\mathrm{p}_0\rangle$, being for example 0.36 and 0.69 for $\langle \mathrm{s}_0|\mathrm{p}_0\rangle = \frac{1}{3}$ in $\bar{\mathrm{p}}$–H and p–H bonds respectively compared with $\frac{1}{3}$ and $\frac{2}{3}$ in the zero-overlap limit.

Since $\bar{\mathrm{p}}$–H and p–H bonds as treated here can be expected to provide a good model for any bond between such a heavy element and a group containing no π electrons and a single unpaired electron in a σ orbital, the bonding characteristics deduced above apply to all such bonds between hard Lewis acid–hard Lewis base pairs. It has been shown that the bonds $\bar{\mathrm{p}}$–g_σ and p–g_σ between a heavy element in its *j–j* coupled ground state and a group g_σ of similar electronegativity will not be greatly weakened compared with their non-relativistic analogues having respective orders of $\frac{2}{3}$ and $\frac{5}{6}$. However, the bond between a heavy element and a group of rather different electronegativity is predicted to be considerably weakened compared with its non-relativistic analogue because only a fraction of the bond can be stabilized by ionic–covalent resonance.

(*c*) *The relativistic molecular orbital description*

(i) *Methodology*

The purpose of this subsection is both to present the fundamentals of the relativistic molecular orbital theory used throughout this paper and to explain and justify the methods used to interpret the bonding described by relativistic molecular orbital wavefunctions.

The multi-electron relativistic molecular orbital wavefunction is built from one-electron molecular orbitals $|\phi_i m\rangle$ which can be expanded in a complete set of Dirac–Fock atomic orbitals, denoted for linear molecules as $|\chi_t m\rangle$:

$$|\phi_i m\rangle = \sum_t c_{ti}|\chi_t m\rangle. \tag{3.28}$$

For nonlinear molecules the molecular orbitals $|\phi_i m\rangle$ cease to carry the label m. The expansion (3.28) is the direct relativistic analogue of the non-relativistic Roothaan scheme (Roothaan 1951) and thus differs from the approach of Kim (1967) in which the large and small components are separately expanded in a basis. However, an expansion of the type (3.28) is equally valid because all the Dirac–Fock atomic orbitals of any atom, both occupied and unoccupied, including those of energy less than $-2c^2$ constitute a complete set. The coefficients c_{ti} are calculated by solving the matrix equation (Roothaan 1951)

$$\boldsymbol{F}_{\mathrm{M}}\boldsymbol{C} = \boldsymbol{S}\boldsymbol{C}\boldsymbol{\mathscr{E}} \tag{3.29}$$

where $\hat{\mathrm{F}}_{\mathrm{M}}$ is the molecular Fock operator having elements $\langle\chi_t|\hat{\mathrm{F}}_{\mathrm{M}}|\chi_u\rangle$, and $\boldsymbol{S}$ is the overlap matrix ($\boldsymbol{S}_{tu} = \langle\chi_t|\chi_u\rangle$). The qualitative features of the bonding are revealed by assuming both that the core orbitals of the individual atoms remain unchanged on formation of the molecule and that the valence molecular orbitals can be expressed solely in terms of the valence orbitals of the constituent atoms. The second assumption parallels that made in the first of the four stages in the Kappa valence method in that overlaps between the core orbitals on one atom with the valence orbitals on another are neglected.

Two different arguments show that the qualitative predictions of chemical bonding made so successfully by non-relativistic molecular orbital theory should not be regarded as based on the simple criterion of the total energy of the N-electron wavefunction. Firstly it is well known that molecular orbital theory cannot be used to construct an entire potential curve because, except in special circumstances, the dissociation process is described incorrectly. Secondly it can be questioned whether the binding energy can be calculated as the difference between the total energy predicted by a molecular Hartree–Fock wavefunction and the sum of the Hartree–Fock energies of the isolated atoms because it is not clear that the molecular energy and the sum of the atomic energies are strictly comparable. Indeed evidence that they are not comparable is provided by the very poor agreement with experiment often shown by dissociation energies calculated by this method, the case of F_2 which is thus predicted to be unbound by 1.63 eV (Wahl 1964) being the most dramatic example. However, it can be strongly argued that simple molecular orbital theory has been so outstandingly successful in explaining chemical bonding because, for small and intermediate internuclear distances, it can correctly predict the forces on the nuclei which, by the Hellmann–Feynman theorem, can be expressed as a sum of orbital contributions that can be simply understood. Approximations, constructed from a small basis of atomic orbitals centred on the nuclei, to the exact Hartree–Fock wavefunction do not satisfy the Hellman–Feynman theorem exactly although it is exactly satisfied by the true Hartree–

Fock function. However, it has been shown by Hurley (1954*a*, *b*, *c*) that the errors arising when this theorem is applied to approximate molecular orbital wavefunctions do not obscure the essential features of the bonding provided that the experimental dissociation products of the multi-electron state under investigation are not ionic. Thus the bonding properties of a molecular orbital depend solely upon the contribution that it makes to the forces on the nuclei. These have been shown (Berlin 1951) to depend solely upon the region of space occupied by the molecular orbital, one concentrating charge between the nuclei in a diatomic molecule being bonding and one concentrating charge behind the nuclei being anti-bonding, thus explaining the success of simple molecular orbital theory.

The discussion of the last paragraph shows that the bonding properties of a relativistic molecular orbital wavefunction should be investigated by examining the charge distribution and applying the ideas of Berlin (1951) and of Bader and coworkers (Bader *et al.* 1967*a*, *b*; Bader & Bardrauk 1968) rather than by attempting to calculate its energy. It must first be shown that the description, provided by non-relativistic theory, of the forces acting upon the nuclei still applies in the relativistic case. The relation (3.3*a*) with $|\psi_{\kappa\mathrm{v}}\rangle$ replaced by the exact N-electron Dirac–Fock wavefunction $|\psi_{\mathrm{MDF}}\rangle$ is satisfied exactly for all nuclear configurations provided the orbitals (2.8) used to construct $\hat{\mathscr{H}}_{\mathrm{Br}}$ are chosen to be the exact Dirac–Fock molecular orbitals denoted $|\phi_{a\mathrm{MDF}}\rangle$. Hence it follows that the proof (Stanton 1962) showing that the exact non-relativistic Hartree–Fock wavefunction for a closed shell system satisfies the Hellmann–Feynman theorem is also valid for the molecular Dirac–Fock function. This result is a straightforward consequence (Stanton 1962) of the relativistic analogue of Brillouin's theorem

$$\langle\psi(a\rightarrow\mathrm{e})|\hat{\mathscr{H}}_{\mathrm{T}}|\psi_{\mathrm{MDF}}\rangle = 0, \tag{3.30}$$

where $|\psi(a\rightarrow\mathrm{e})\rangle$ is the singly excited determinant constructed by replacing the orbital $|\phi_{a\mathrm{MDF}}\rangle$ occupied in $|\psi_{\mathrm{MDF}}\rangle$ by the unoccupied orbital $|\phi_{\mathrm{eMDF}}\rangle$, which is an immediate consequence of (2.8). It should be noted that although the sum of Dirac spinors used to express the derivative $\partial|\phi_{a\mathrm{MDF}}\rangle/\partial\lambda$, where λ is a nuclear coordinate, will contain both electron- ($\epsilon > -2c^2$) and position- ($\epsilon < -2c^2$) like solutions of (2.8), the relation (3.30) is satisfied by all $|\psi(a\rightarrow\mathrm{e})\rangle$ regardless of the eigenvalue ϵ_{e}. Application of the Hellmann–Feynman theorem to a diatomic molecule having nuclei μ and μ' shows that the z-component of the force ($F_{z,\mu}$) acting on nucleus μ is given by

$$\begin{aligned} F_{z,\mu} &= -\left(\frac{\partial\langle\psi_{\mathrm{MDF}}|\hat{\mathscr{H}}_{\mathrm{Br}}|\psi_{\mathrm{MDF}}\rangle}{\partial r_{z,\mu}}\right)_{z_{\mu'}} \\ &= \mp Z_\mu Z_{\mu'}/R^2 - Z_\mu \sum_{a\in\psi_{\mathrm{MDF}}}\sum_{q=1}^{4}\int \phi_{a,q}(r_1)^*\, z_{1\mu}\,\phi_{a,q}(r_1)\,\mathrm{d}r_1, \end{aligned} \tag{3.31}$$

where $z_{1\mu}$ and $r_{1\mu}$ are measured relative to nucleus μ as origin. The positive sign is taken in (3.31) if the z-coordinate of nucleus μ' is less than that of nucleus μ, and the negative sign if it is greater, the sum over a is over all the occupied Dirac–Fock molecular orbitals, and q is the spinor index so that the integration over $\boldsymbol{r}_1$ is purely spatial.

The bonding properties of a relativistic molecular orbital wavefunction can be investigated by replacing $\phi_{a\mathrm{MDF}}$ in (3.31) by the approximate molecular orbitals calculated according to the prescription presented at the end of the first paragraph of this section because the errors arising from applying the Hellmann–Feynman theorem to an approximation to $|\psi_{\mathrm{MDF}}\rangle$ do not obscure the qualitative features (Hurley 1954*c*). In this approximation the core orbitals of atom μ, which contain a total of $N_{c,\mu}$ electrons, are assumed to be unchanged upon molecule formation. In the calculation of the force $F_{z,\mu}$ predicted in this approximation, the contributions of the core orbitals ($|c_\mu\rangle$) of atom μ vanish while the total contribution of all the core orbitals ($|c_{\mu'}\rangle$) of atom μ' is $N_{c,\mu'}/R^2$ which merely cancels the repulsive force arising from $N_{c,\mu}$, units of charge of the nucleus μ'. These force contributions show (Bader *et al.* 1967*a*) that the core orbitals do not contribute to the bonding. It should be pointed out that, for the core orbitals, the contributions of the small components, which are the terms in (3.31) having $q = 3$ and $q = 4$, cannot be neglected because a significant fraction of the electron density resides in the small components. For the 1s orbital in E113, for example, the norm $(\int_0^\infty Q_{1s}^2(r)\,dr)$ of the small components is 0.21.

For the valence molecular orbitals, unlike the core orbitals, the contributions of the small components to the forces (3.31) can be neglected because they are smaller by a factor of c^2 than those made by the large components. This shows that the bonding properties of valence relativistic molecular orbitals are determined by those of the large components. This conclusion coupled with the observation that the core orbitals are strictly non-bonding establishes the key result used throughout this paper that the bonding characteristics of relativistic molecular orbital wavefunctions are determined by the bonding properties of the large components of the valence molecular orbitals.

(ii) *Bonding in hydrides*

In this subsection the purely covalent bonding between a hydrogen atom and a heavy element containing a single electron in a $\bar{p}$ or a p orbital outside closed subshells is investigated by using the relativistic molecular orbital method. This problem is reconsidered even though it was cleanly solved by using the Kappa valence method because both the molecular orbital and Kappa valence approaches are approximations which, in the same way as do non-relativistic molecular orbital and valence bond theories, represent two extreme viewpoints. Hence one can have almost complete confidence if both the relativistic molecular orbital and Kappa valence methods make the same prediction, while such confidence is hardly possible if only one of the two approaches has been examined.

A purely covalent bond between a hydrogen atom and a heavy element having a large energy separation between the valence $\bar{p}$ and p orbitals is described in relativistic molecular orbital theory by the wavefunction

$$|\psi_{\text{MO}}\rangle = \hat{\mathscr{A}}[|\text{core}\rangle|\phi\tfrac{1}{2}\rangle|\phi-\tfrac{1}{2}\rangle]. \tag{3.32}$$

Here $|\phi\frac{1}{2}\rangle$ is the bonding molecular orbital which is expressed as a linear combination of the two atomic orbitals $|v\frac{1}{2}\rangle$ and $|s\frac{1}{2}\rangle$. The atomic Dirac–Fock equations (3.7) show that the two diagonal elements $\langle v\frac{1}{2}|\hat{F}_M|v\frac{1}{2}\rangle$ and $\langle s\frac{1}{2}|\hat{F}_M|s\frac{1}{2}\rangle$ of the molecular Fock operator can be expressed as

$$\left.\begin{aligned}\langle v\tfrac{1}{2}|\hat{F}_M|v\tfrac{1}{2}\rangle &= \epsilon_v + \langle v\tfrac{1}{2}|\hat{V}_H + \hat{V}_{\text{val}}|v\tfrac{1}{2}\rangle,\\ \langle s\tfrac{1}{2}|\hat{F}_M|s\tfrac{1}{2}\rangle &= E_H + \langle s\tfrac{1}{2}|\hat{V}_{\text{NE}} + \hat{V}_{\text{DFE}} + \hat{V}_{\text{val}}|s\tfrac{1}{2}\rangle\end{aligned}\right\} \tag{3.33}$$

because

$$\hat{F}_M = \hat{\mathscr{H}}_{\text{k.e.}} + \hat{V}_{\text{NE}} + \hat{V}_{\text{DFE}} + \hat{V}_H + \hat{V}_{\text{val}} \tag{3.34}$$

where $\hat{V}_{\text{val}}$ is the sum of the coulomb and exchange potentials generated by the orbitals $|\phi\frac{1}{2}\rangle$ and $|\phi-\frac{1}{2}\rangle$. There is a small ambiguity in defining purely covalent bonding because it can be argued that this implies either that the energies of the isolated valence orbitals are equal (i.e. $\epsilon_{\mathrm{v}} = E_{\mathrm{H}}$) or that the energies of the atomic orbitals in the molecular environment are equal (i.e. $\langle \mathrm{v}\tfrac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{v}\tfrac{1}{2}\rangle = \langle \mathrm{s}\tfrac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{s}\tfrac{1}{2}\rangle$). However, this ambiguity is not important because the difference between the molecular terms in the two matrix elements (3.33) will be small and consequently one can take these two matrix elements to be equal without contradicting the assumption that the bonding is purely covalent. With this assumption the bonding molecular orbital $|\phi\tfrac{1}{2}\rangle$ becomes

$$|\phi\tfrac{1}{2}\rangle = \tfrac{1}{\sqrt{2}}\, S_{\mathrm{MO}}(\mp|\mathrm{v}\tfrac{1}{2}\rangle + |\mathrm{s}\tfrac{1}{2}\rangle), \tag{3.35}$$

$$S_{\mathrm{MO}} = (1 \mp \langle \mathrm{v}\tfrac{1}{2}|\mathrm{s}\tfrac{1}{2}\rangle)^{-\frac{1}{2}}, \tag{3.36}$$

where the z-coordinate of the proton is greater than that of the nucleus of the heavy element, and the negative sign is taken for a $\bar{\mathrm{p}}$ orbital and the positive sign for a p one. The molecular orbital $|\phi -\tfrac{1}{2}\rangle$ is degenerate with $|\phi\tfrac{1}{2}\rangle$ from which it can be generated by using (2.18).

The results of the last §3 (ci) show that the bonding properties of the wavefunction (3.32) are determined by those of the large components $|\phi\tfrac{1}{2}\rangle_{\mathrm{L}}$ of the valence molecular orbital $|\phi\tfrac{1}{2}\rangle$. The expressions (3.9) show that these large components are

$$|\phi\tfrac{1}{2}\rangle_{\mathrm{L}} = S_{\mathrm{MO}}\tfrac{1}{\sqrt{2}}[|(\sqrt{a}\mathrm{p}_0 + \mathrm{s}_0)\,\alpha\rangle \mp (1-a)^{\frac{1}{2}}\,|\mathrm{p}_1\,\beta\rangle], \tag{3.37a}$$

$$S_{\mathrm{MO}} = (1 + \sqrt{a}\langle \mathrm{s}_0|\mathrm{p}_0\rangle)^{-\frac{1}{2}}. \tag{3.37b}$$

Substituting (3.37a) into (3.31), and then noting that the core subshells are assumed to have negligible densities at distances from the nucleus of the heavy element greater than R, show that the forces $F_{z,\,\mathrm{E}}$ and $F_{z,\,\mathrm{H}}$ on the nucleus of the heavy element and the proton are given by

$$F_{z,\,\mathrm{E}} = -R^{-2} - 2(1+\sqrt{a}\langle \mathrm{s}_0|\mathrm{p}_0\rangle)^{-1}\,(\tfrac{1}{2}\langle \mathrm{s}_0|z_{\mathrm{E}}/r_{\mathrm{E}}^3|\mathrm{s}_0\rangle + \sqrt{a}\langle \mathrm{s}_0|z_{\mathrm{E}}/r_{\mathrm{E}}^3|\mathrm{p}_0\rangle), \tag{3.38a}$$

$$F_{z,\,\mathrm{H}} = R^{-2} - 2(1+\sqrt{a}\langle \mathrm{s}_0|\mathrm{p}_0\rangle)^{-1}\,[\tfrac{1}{2}(1-a)\,\langle \mathrm{p}_1|z_{\mathrm{H}}/r_{\mathrm{H}}^3|\mathrm{p}_1\rangle + \tfrac{1}{2}a\langle \mathrm{p}_0|z_{\mathrm{H}}/r_{\mathrm{H}}^3|\mathrm{p}_0\rangle + \sqrt{a}\langle \mathrm{s}_0|z_{\mathrm{H}}/r_{\mathrm{H}}^3|\mathrm{p}_0\rangle]. \tag{3.38b}$$

Here z_{E}, z_{H}, r_{E} and r_{H} are defined as $z_{1,\,\mu}$ and $r_{1,\,\mu}$ in (3.31). The results (3.38) show that, for internuclear distances R greater than the equilibrium internuclear separation but sufficiently small that the atoms interact significantly, the contributions to the forces arising from the one-centre densities merely balance the repulsive force ($\mp 1/R^2$) between the proton and the nucleus plus the core of the heavy element if the normalization factor S_{MO} does not deviate significantly from unity. It is the terms in (3.38a) and (3.38b) constructed from the overlap charge density $\mathrm{p}_0(r)\,\mathrm{s}_0(r)$ that are responsible for the attractive force between the nuclei and hence the binding. Although both the forces $F_{z,\,\mathrm{E}}$ and $F_{z,\,\mathrm{H}}$ must vanish at the equilibrium internuclear distance, the binding can still be attributed to the overlap charge density (Bader *et al.* 1967a) because the force contribution arising from this density exactly counterbalances the repulsive force arising from the nuclei, core orbitals and one-centre density terms. The one-centre density contributions to the forces in (3.38) only fail to counterbalance the repulsive force ($\mp 1/R^2$) between the proton and the nucleus plus the core of the heavy element because the presence of the overlap charge density causes the normalization constant S_{MO} to be less than unity. These results show that there are no specifically anti-bonding effects and that the bonding, which is purely covalent by virtue of the equality of the coefficients of $|\mathrm{v}\tfrac{1}{2}\rangle$ and $|\mathrm{s}\tfrac{1}{2}\rangle$ in $|\phi\tfrac{1}{2}\rangle$ can be attributed to the overlap density which occupies the binding spatial regions (Berlin 1951). This suggests very strongly that covalent $\bar{\mathrm{p}}$–H bonds are weaker than p–H ones because the coefficients multiplying the similar overlap densities in (3.38) are $\tfrac{2}{\sqrt{3}}(1+\tfrac{1}{\sqrt{3}}\langle \mathrm{s}_0|\mathrm{p}_0\rangle)^{-1}$ and $2\sqrt{\tfrac{2}{3}}(1+\sqrt{\tfrac{2}{3}}\langle \mathrm{s}_0|\mathrm{p}_0\rangle)^{-1}$ respectively. Furthermore these bonds are predicted to be weaker than a normal covalent σ bond because in the $\bar{p}$ and p cases the respective fractions $\frac{1}{3}S_{MO}^2$ and $\frac{1}{6}S_{MO}^2$ of the density which arise from the π components of $|v\tfrac{1}{2}\rangle_L$ do not contribute to the bonding whereas in a normal covalent bond the entire density is available to participate in the bonding.

It can be very seriously questioned whether the strengths of $\bar{p}$–H, p–H and normal σ covalent bonds can be related more quantitatively by comparing the coefficients multiplying the overlap densities. This approach would fail to disentangle the real bond order changes caused by the differing fractions of the density possessing σ spatial symmetry from the very probably spurious ones predicted solely because the ratio of the p_0 function and the hydrogen s orbital in (3.37) changes. Thus the order of the normal σ bond formed by placing two electrons in the normalized orbital $c_1 p_0 + c_2 s$ would be predicted to depend on the coefficients c_1 and c_2 were it taken to be $2c_1c_2$, a fully ionic bond being predicted to have zero order. This shows that the orders of $\bar{p}$–H and p–H bonds can only be reliably calculated by isolating the fraction of the density that can be held responsible for the binding and confirming that this fraction can be regarded as fully bonding with respect to those portions of the nuclear charges that can be regarded as bound by it. Since firstly the bonding is purely covalent and secondly the fractions $\frac{1}{3}S_{MO}^2$ and $\frac{1}{6}S_{MO}^2$ of the density in the $\bar{p}$ and p cases respectively, which arise from the π components of $|v\pm\tfrac{1}{2}\rangle_L$, do not contribute to the overlap charge distribution, these fractions do not contribute to the bonding. Hence the bonding arises from the remaining fractions ($1-\frac{1}{3}S_{MO}^2$ and $1-\frac{1}{6}S_{MO}^2$ in the $\bar{p}$ and p cases respectively) of the densities that have purely σ symmetry. Thus molecular orbital theory predicts the orders of $\bar{p}$–H and p–H bonds to be $1-\frac{1}{3}S_{MO}^2$ $(=(2+\sqrt{3}\langle s_0|p_0\rangle)/(3+\sqrt{3}\langle s_0|p_0\rangle))$ and $1-\frac{1}{6}S_{MO}^2$ $(=(5+2\sqrt{6}\langle s_0|p_0\rangle)/(6+2\sqrt{6}\langle s_0|p_0\rangle))$ respectively which are qualitatively similar to those of $(2+\sqrt{3}\langle s_0|p_0\rangle^2)/(3+\sqrt{3}\langle s_0|p_0\rangle^2)$ and $(5+2\sqrt{6}\langle s_0|p_0\rangle^2)/(6+2\sqrt{6}\langle s_0|p_0\rangle^2)$ predicted by the Kappa valence method. Furthermore both relativistic molecular orbital and Kappa valence theories agree in predicting the orders of $\bar{p}$–H and p–H bonds to be $\frac{2}{3}$ and $\frac{5}{6}$ in the limit of small overlap $\langle s_0|p_0\rangle$.

It can only be concluded that this approach, in which just the π symmetry portion of $|\phi\tfrac{1}{2}\rangle_L$ is regarded as not fully bonding, is not too simplistic if it can be shown that the entire σ symmetry portion of $|\phi\tfrac{1}{2}\rangle_L$ can after renormalization be regarded as fully bonding. The argument is most simply presented by taking the normalization constant S_{MO} to be unity. The bond order is $\frac{1}{2}$ for H_2^+ where occupation of a fully bonding molecular orbital by one electron binds two nuclei of unit charge. The bond order in the system having the same total nuclear charge of two in which one electron binds a nucleus of charge z_1 to one of charge z_2 $(=2-z_1)$ is $\frac{1}{2}z_1z_2$. Consideration of the limit in which one of the nuclear charges is zero shows that the bond order in this more general system of which H_2^+ is a special case cannot be independent of z_1 and does not therefore remain $\frac{1}{2}$. Occupation by one electron of the molecular orbital (3.39*a*), which is normalized even if overlap is not neglected, binds a nucleus of charge $\frac{6}{5}$ to one of charge $\frac{4}{5}$, the order of the bond that has no ionic character being $\frac{1}{2}(\frac{24}{25})$. Similarly a bond of no net ionic character having an order of $\frac{1}{2}(\frac{120}{121})$ is formed when occupation of the molecular orbital (3.39*b*) by one electron binds a nucleus of charge $\frac{12}{11}$ to one of charge $\frac{10}{11}$:

$$\sigma_p = \left(1+\tfrac{\sqrt{3}}{2}\langle s_0|p_0\rangle\right)^{-\frac{1}{2}}\tfrac{1}{2}(p_0+\sqrt{3}s_0), \tag{3.39a}$$

$$\sigma_p = \left(1+\tfrac{2}{5}\sqrt{6}\langle s_0|p_0\rangle\right)^{-\frac{1}{2}}\tfrac{1}{\sqrt{5}}(\sqrt{2}p_0+\sqrt{3}s_0). \tag{3.39b}$$

Simple electrostatic scaling arguments show that if the magnitudes of the charges of both the nuclei and the electron are reduced by a factor of x, then the bond energy and bond order are reduced by a factor of x^2. This result taken in conjunction with the deduced orders of the one-electron bonds of the above two systems shows that a bond of order $\frac{1}{3}$ is formed when a proton is bound to a nucleus of charge $\frac{2}{3}$ by occupation of the molecular orbital (3.39a) by $\frac{5}{6}$ of an electron. Similarly, the binding of a proton to a nucleus of charge $\frac{5}{6}$ by occupation of the molecular orbital (3.39b) by $\frac{11}{12}$ of an electron yields a bond of order $\frac{5}{12}$. It has already been shown that when the molecular orbital $|\phi\frac{1}{2}\rangle$ is occupied by one electron the π symmetry portion of $|\phi\frac{1}{2}\rangle_L$ can in the $\bar{p}$ and p cases be regarded as counterbalancing the effects of $\frac{1}{3}$ and $\frac{1}{6}$ respectively of a unit of core charge. It then follows that the bonding characteristics of the singly charged positive ion of electronic configuration $|\text{core}\rangle|\phi\frac{1}{2}\rangle$ are similar to those of the two systems in which nuclei of respective charges $\frac{2}{3}$ and $\frac{5}{6}$ are bound to a proton because the σ symmetry portion of the density $(\phi\frac{1}{2})^+_L(\phi\frac{1}{2})_L$ responsible for the bonding is identical to that generated by the appropriate fractional occupation of the molecular orbitals (3.39). Hence the bond order in the singly charged positive ions $|\text{core}\rangle|\phi\frac{1}{2}\rangle$ is $\frac{1}{3}$ if $|v\frac{1}{2}\rangle$ is a $\bar{p}$ orbital while it is $\frac{5}{12}$ if $|v\frac{1}{2}\rangle$ is a p orbital. Consequently the orders of the $\bar{p}$–H and p–H bonds (3.32) formed by the occupation of both the bonding molecular orbitals $|\phi\frac{1}{2}\rangle$ and $|\phi-\frac{1}{2}\rangle$ are $\frac{2}{3}$ and $\frac{5}{6}$ in the $\bar{p}$ and p cases respectively. This confirms that the orders of the bonds (3.32) can indeed be calculated by simply isolating the fraction of the density that by virtue of its π symmetry is non-bonding. If overlap is not neglected in (3.38) then the fractions $\frac{1}{3}S^2_{\text{MO}}$ and $\frac{1}{6}S^2_{\text{MO}}$ of the density having π symmetry counterbalance the same number of units of charge on the proton leaving occupation of the non-normalized molecular orbitals $(1-\frac{1}{3}S^2_{\text{MO}})^{\frac{1}{2}}\,\sigma_p$ and $(1-\frac{1}{6}S^2_{\text{MO}})^{\frac{1}{2}}\,\sigma_p$ to bind the remaining charges. It follows from the arguments given before equation (3.39) that the bond orders are $(1-\frac{1}{3}S^2_{\text{MO}})$ and $(1-\frac{1}{6}S^2_{\text{MO}})$ thus justifying the methods used in the last paragraph.

(iii) *Relation to the Kappa valence method*

The relation between the N-electron relativistic molecular orbital and Kappa valence wavefunctions is revealed by expressing the large components of the valence part of (3.32) in terms of corresponding non-relativistic configurations. With the introduction of the configurations built from the orbitals (3.39a) and (3.39b) for the respective cases where $|v\rangle$ is a $\bar{p}$ or a p orbital,

$$\left.\begin{aligned}
|{}^1\sigma^2\rangle &= |\hat{\mathscr{A}}(\sigma\sigma\alpha\beta)\rangle,\\
|{}^3(\sigma\pi_{-1})_1\rangle &= |\hat{\mathscr{A}}(\sigma p_{-1}\,\alpha\alpha)\rangle,\\
|{}^3(\sigma\pi_1)_{-1}\rangle &= |\hat{\mathscr{A}}(\sigma p_1\,\beta\beta)\rangle,\\
|{}^3(\pi_{-1}\,\pi_1)_0\rangle &= |\tfrac{1}{\sqrt{2}}(p_{-1}p_1-p_1p_{-1})\tfrac{1}{\sqrt{2}}(\alpha\beta+\beta\alpha)\rangle,\\
|{}^1\pi^2\rangle &= |\tfrac{1}{\sqrt{2}}(p_{-1}p_1+p_1p_{-1})\tfrac{1}{\sqrt{2}}(\alpha\beta-\beta\alpha)\rangle,
\end{aligned}\right\}\tag{3.40}$$

the large components of $|\psi_{\text{MO}}\rangle$ for the $\bar{p}$ and p cases are

$$\begin{aligned}
|\psi_{\bar{p}\text{MO}}\rangle_L = &-(1-\tfrac{1}{3}S^2_{\text{MO}})\,|{}^1\sigma^2\rangle+\tfrac{1}{\sqrt{3}}S_{\text{MO}}(1-\tfrac{1}{3}S^2_{\text{MO}})^{\frac{1}{2}}\,[|{}^3(\sigma\pi_{-1})_1\rangle-|{}^3(\sigma\pi_1)_{-1}\rangle]\\
&+\tfrac{1}{3\sqrt{2}}S^2_{\text{MO}}[|{}^3(\pi_{-1}\,\pi_1)_0\rangle+|{}^1\pi^2\rangle],
\end{aligned}\tag{3.41a}$$

$$\begin{aligned}
|\psi_{p\text{MO}}\rangle_L = &\ (1-\tfrac{1}{6}S^2_{\text{MO}})\,|{}^1\sigma^2\rangle+\tfrac{1}{\sqrt{6}}S_{\text{MO}}(1-\tfrac{1}{6}S^2_{\text{MO}})^{\frac{1}{2}}\,[|{}^3(\sigma\pi_{-1})_1\rangle-|{}^3(\sigma\pi_1)_{-1}\rangle]\\
&-\tfrac{1}{6\sqrt{2}}S^2_{\text{MO}}[|{}^3(\pi_{-1}\,\pi_1)_0\rangle+|{}^1\pi^2\rangle],
\end{aligned}\tag{3.41b}$$

from which the zero overlap limits are obtained by setting $S_{\text{MO}} = 1$. Since it has been shown that the orbitals (3.39) should be regarded as fully bonding while the π orbitals are non-bonding, the formal bond orders in the configurations σ^2, $\sigma\pi$ and π^2 can be taken to be 1, $\frac{1}{2}$

and zero respectively. The total orders of the bonds in (3.41) are predicted, by weighting the bond orders contributed by each configuration (3.40) by the square of the coefficient, multiplying it and forming the sum, to be $1-\frac{1}{3}S_{\mathrm{MO}}^2$ and $1-\frac{1}{6}S_{\mathrm{MO}}^2$ in agreement with the previous results.

The mechanism of the bonding in the relativistic molecular orbital and Kappa valence approaches appears to be rather different because the π symmetry portion of $|\mathrm{v}\frac{1}{2}\rangle_{\mathrm{L}}$ is non-bonding in the former approach while it makes an important contribution to the bonding in the latter. Nevertheless the difference is not as great as suggested by this observation because the bonding described by the molecular orbital function is similar to that predicted by the Kappa valence one in that both methods predict the bond to be composed of a mixture of a normal singlet σ covalent contribution having a bond order of unity and a triplet contribution arising from a wavefunction having Π symmetry which has a bond order of $\frac{1}{2}$. However, although both approaches predict identical total bond orders in the zero-overlap limit, the individual ${}^1\sigma$ and ${}^3\Pi$ contributions are not identical. Thus for $\bar{\mathrm{p}}$–H bonds the Kappa valence method predicts the bonding to be $\frac{1}{3}{}^1\sigma$ and $\frac{2}{3}{}^3\Pi$ while the relativistic molecular orbital approach predicts both these fractions to be $\frac{4}{9}$ with the remaining $\frac{1}{9}$ of the wavefunction being formally non-bonding. In p–H bonds the Kappa valence approach predicts $\frac{2}{3}{}^1\sigma$ and $\frac{1}{3}{}^3\Pi$ bonding while the relativistic molecular orbital method predicts these fractions to be $\frac{25}{36}$ and $\frac{5}{18}$ respectively.

It should be pointed out that the ratios of 1:2 and 1:5 in the $\bar{\mathrm{p}}$ and p cases respectively of the contributions made to the bond order by the ${}^3\Pi$ and ${}^1\Sigma$ functions is independent of the order assigned to the bond formed by double occupation of the molecular orbitals (3.39). It is shown in Appendix 4 that the predicted orders of the $\bar{\mathrm{p}}$–H and p–H bonds are not greatly changed if a different much weaker assumption is made about the order of such a bond. It should also be pointed out that relativistic molecular orbital theory quite unambiguously predicts that the portion of the large components of the wavefunction (3.32) that has ${}^3\Pi$ symmetry contributes to the bonding without any assumptions being made beyond those standard in molecular orbital theory.

4. Bonding in dihydrides

(a) *The Kappa valence description of* p² *dihydrides*

The only heavy elements capable of forming more than one covalent bond without the need to invoke a valence state in which $\bar{\mathrm{p}}$ electrons are partially promoted into p orbitals are those of group VIB whose electronic configurations in the limit of large $\bar{\mathrm{p}} \rightarrow \mathrm{p}$ excitation energies are $\bar{\mathrm{p}}^2\mathrm{p}^2$. It is shown in the next section that the ground $\bar{\mathrm{p}}^2$ closed-shell configurations of heavy group-IVB elements cannot form covalent bonds while heavy group VIIB elements are restricted to forming just a single covalent bond because their ground $\bar{\mathrm{p}}^2\mathrm{p}^3$ configurations have only one electron less than the $\bar{\mathrm{p}}^2\mathrm{p}^4$ inert gas configuration. In this section the Kappa valence method is used to investigate the covalent bonding in group VIB dihydrides. It will be assumed both that the $\bar{\mathrm{p}}$ electrons are so tightly bound that they can be regarded as belonging to the core and that the energy separation between the two levels of the p^2 configuration having total angular momenta (J) of 0 and 2 is negligible. The qualitative features of the results apply to the bonding between a group VIB element in the $\bar{\mathrm{p}}^2\mathrm{p}^2$ configuration and any two ligands each of which has no π electrons and a single unpaired electron occupying a σ orbital.

Although group theoretical arguments can neither reveal every detail of the bonding in group VIB dihydrides nor predict the molecular geometry, they nevertheless determine several essential features of the Kappa valence wavefunction. Thus the bond between a hydrogen atom and one hybrid denoted $|\mathrm{t}_1\rangle$ constructed from the four Dirac–Fock p orbitals of the heavy element (E) cannot be described by the single product $|\mathrm{t}_1\rangle(c_3|\mathrm{s}_1\tfrac{1}{2}\rangle+c_4|\mathrm{s}_1-\tfrac{1}{2}\rangle)$ because this does not have the correct symmetry properties under the operation $\hat{\mathrm{H}}_{y,\mathrm{t}}$ (2.19) corresponding to reflexion in the molecular (xz) plane. It is therefore necessary to introduce the three further hybrids defined by

$$\left.\begin{aligned}|\mathrm{t}_2\rangle &= \hat{\mathrm{H}}_{y,\mathrm{t}}|\mathrm{t}_1\rangle,\\ |\mathrm{t}_3\rangle &= -\mathrm{i}\hat{\mathrm{H}}_{z,\mathrm{t}}|\mathrm{t}_1\rangle,\\ |\mathrm{t}_4\rangle &= \hat{\mathrm{H}}_{y,\mathrm{t}}|\mathrm{t}_3\rangle\end{aligned}\right\} \tag{4.1}$$

from which the relation

$$-\mathrm{i}\hat{\mathrm{H}}_{z,\mathrm{t}}|\mathrm{t}_2\rangle = -|\mathrm{t}_4\rangle \tag{4.2}$$

is established by expressing $|\mathrm{t}_2\rangle$ in terms of $|\mathrm{t}_1\rangle$ and invoking $\hat{\mathrm{H}}_{z,\mathrm{t}}\hat{\mathrm{H}}_{y,\mathrm{t}} = -\hat{\mathrm{H}}_{y,\mathrm{t}}\hat{\mathrm{H}}_{z,\mathrm{t}}$. The definitions (4.1) and relation (4.2), taken in conjunction with the results from (2.30) and (2.31),

$$\hat{\mathrm{H}}_{y,\mathrm{t}}|\mathrm{s}_\mu\tfrac{1}{2}\rangle = -|\mathrm{s}_\mu-\tfrac{1}{2}\rangle,\quad \hat{\mathrm{H}}_{y,\mathrm{t}}|\mathrm{s}_\mu-\tfrac{1}{2}\rangle = |\mathrm{s}_\mu\tfrac{1}{2}\rangle,\quad \mu = 1,2, \tag{4.3}$$

$$\hat{\mathrm{H}}_{z,\mathrm{t}}|\mathrm{s}_\mu\tfrac{1}{2}\rangle = \mathrm{i}|\mathrm{s}_{\mu'}\tfrac{1}{2}\rangle,\quad \hat{\mathrm{H}}_{z,\mathrm{t}}|\mathrm{s}_\mu-\tfrac{1}{2}\rangle = -\mathrm{i}|\mathrm{s}_{\mu'}-\tfrac{1}{2}\rangle,\quad \mu = 1,\ \mu' = 2,\quad \text{and}\quad \mu = 2,\ \mu' = 1, \tag{4.4}$$

show that the wavefunction

$$\begin{aligned}|\psi_{\kappa\mathrm{v}}\rangle = S\hat{\mathscr{A}}\{|\mathrm{core}\rangle\tfrac{1}{\sqrt{2}}[|\mathrm{t}_1\rangle(c_3|\mathrm{s}_1\tfrac{1}{2}\rangle+c_4|\mathrm{s}_1-\tfrac{1}{2}\rangle)-|\mathrm{t}_2\rangle(-c_4|\mathrm{s}_1\tfrac{1}{2}\rangle+c_3|\mathrm{s}_1-\tfrac{1}{2}\rangle)]\\ \times\tfrac{1}{\sqrt{2}}[|\mathrm{t}_3\rangle(c_3|\mathrm{s}_2\tfrac{1}{2}\rangle-c_4|\mathrm{s}_2-\tfrac{1}{2}\rangle)-|\mathrm{t}_4\rangle(c_4|\mathrm{s}_2\tfrac{1}{2}\rangle+c_3|\mathrm{s}_2-\tfrac{1}{2}\rangle)]\},\end{aligned} \tag{4.5}$$

is totally symmetric under both $\hat{\mathrm{H}}_{y,\mathrm{T}}$ and $\hat{\mathrm{H}}_{z,\mathrm{T}}$. Here S is a normalization constant which becomes unity if all orbital overlaps vanish. The factor of $-\mathrm{i}$ in the definition of $|\mathrm{t}_3\rangle$, (4.1), has no fundamental significance being merely introduced so that the four coefficients of the orbitals $|\mathrm{p}m\rangle$ in $|\mathrm{t}_3\rangle$ are real if those, (4.6), in $|\mathrm{t}_1\rangle$ have this property. Comparison of (4.5) with the wavefunction (3.1) shows that the first term in square brackets in (4.5) describes a Kappa valence bond between the heavy element and the first hydrogen atom while the second square-bracketed term describes a similar bond to the second hydrogen atom. These two bonds are entirely equivalent being interconverted by the operator $\hat{\mathrm{H}}_{z,\mathrm{t}}$ corresponding to reflexion in the xy-plane. For the general case in which the dihydride is nonlinear, the wavefunction cannot be specified more precisely by purely group theoretical arguments, in contrast to the monohydrides discussed in §3 for which the homopolar Kappa valence wavefunction was symmetry determined.

Further details of the bonding in dihydrides can only be deduced by determining the form of the hybrids $|\mathrm{t}_i\rangle$ more explicitly. By expressing $|\mathrm{t}_1\rangle$ as

$$|\mathrm{t}_1\rangle = d_1|\mathrm{p}\tfrac{1}{2}\rangle+d_2|\mathrm{p}\tfrac{3}{2}\rangle+d_3|\mathrm{p}-\tfrac{1}{2}\rangle+d_4|\mathrm{p}-\tfrac{3}{2}\rangle \tag{4.6a}$$

with

$$d_1^2+d_2^2+d_3^2+d_4^2 = 1, \tag{4.6b}$$

where the coefficients d_i are to be determined, and then explicitly constructing $|\mathrm{t}_2\rangle$, $|\mathrm{t}_3\rangle$ and $|\mathrm{t}_4\rangle$ from (4.6a) by using (4.1) and the results (2.30) and (2.31) that

$$\left.\begin{aligned}\hat{\mathrm{H}}_{y,\mathrm{t}}|\mathrm{p}\pm\tfrac{1}{2}\rangle &= \mp|\mathrm{p}\mp\tfrac{1}{2}\rangle, & \hat{\mathrm{H}}_{y,\mathrm{t}}|\mathrm{p}\pm\tfrac{3}{2}\rangle &= \pm|\mathrm{p}\mp\tfrac{3}{2}\rangle,\\ -\mathrm{i}\hat{\mathrm{H}}_{z,\mathrm{t}}|\mathrm{p}\pm\tfrac{1}{2}\rangle &= \mp|\mathrm{p}\pm\tfrac{1}{2}\rangle, & -\mathrm{i}\hat{\mathrm{H}}_{z,\mathrm{t}}|\mathrm{p}\pm\tfrac{3}{2}\rangle &= \pm|\mathrm{p}\pm\tfrac{3}{2}\rangle,\end{aligned}\right\} \tag{4.7}$$

it follows that

$$\langle\mathrm{t}_1|\mathrm{t}_2\rangle = \langle\mathrm{t}_3|\mathrm{t}_4\rangle = 0, \tag{4.8}$$

for all values of d_i. Hence further conditions are needed to fix the coefficients in (4.6). By direct analogy with the hybrids used to describe bonding in non-relativistic theory, such as the well known sp³ tetrahedral ones, the four hybrids $|\mathrm{t}_i\rangle$ will be chosen to be orthogonal, thus ensuring that the two Kappa valence bonds in (4.5) are essentially independent. Thus imposing the two conditions

$$\langle \mathrm{t}_1|\mathrm{t}_3\rangle = \langle \mathrm{t}_1|\mathrm{t}_4\rangle = 0 \tag{4.9}$$

ensures that all four hybrids are orthogonal because it follows from these relations and (4.1), by noting that $\hat{\mathrm{H}}^2_{y,\,\mathrm{t}} = -1$, that

$$\langle \mathrm{t}_2|\mathrm{t}_3\rangle = \langle \mathrm{t}_2|\mathrm{t}_4\rangle = 0. \tag{4.10}$$

The first of the conditions (4.9), which becomes $-d_1^2+d_2^2+d_3^2-d_4^2 = 0$ after substitution for $|\mathrm{t}_1\rangle$ and $|\mathrm{t}_3\rangle$ by using (4.6*a*), (4.1) and (4.7), shows when taken in conjunction with (4.6*b*) that $d_1^2+d_4^2 = d_2^2+d_3^2 = \frac{1}{2}$. This result taken in conjunction with the second condition (4.9), which becomes $d_1d_3+d_2d_4 = 0$ after substitution for $|\mathrm{t}_1\rangle$ and $|\mathrm{t}_4\rangle$, shows that $d_1 = \pm d_2$ and $d_3 = \mp d_4$. Although the hybrids have not been uniquely defined, it is clear that one chooses $d_1 = -d_2$ and hence $d_3 = d_4$ so that each hybrid points towards the hydrogen atom to which it is bonded in the wavefunction (4.5) rather than away from it. Hence defining the hybrids

$$\left.\begin{aligned}
|\chi_1\rangle &= \tfrac{1}{\sqrt{2}}\,(|\mathrm{p}\tfrac{1}{2}\rangle - |\mathrm{p}\tfrac{3}{2}\rangle),\\
|\chi_2\rangle &= -\tfrac{1}{\sqrt{2}}\,(|\mathrm{p}-\tfrac{1}{2}\rangle + |\mathrm{p}-\tfrac{3}{2}\rangle),\\
|\chi_3\rangle &= -\tfrac{1}{\sqrt{2}}\,(|\mathrm{p}\tfrac{1}{2}\rangle + |\mathrm{p}\tfrac{3}{2}\rangle),\\
|\chi_4\rangle &= \tfrac{1}{\sqrt{2}}\,(|\mathrm{p}-\tfrac{1}{2}\rangle - |\mathrm{p}-\tfrac{3}{2}\rangle),
\end{aligned}\right\} \tag{4.11}$$

which obey relations exactly analogous to (4.1) and (4.2), any wavefunction (4.5) constructed from hybrids (4.1) satisfying the orthogonality conditions (4.9) can be written

$$\begin{aligned}
|\psi_{\kappa\mathrm{v}}\rangle = S\hat{\mathscr{A}}\{&|\mathrm{core}\rangle\\
&\times \tfrac{1}{\sqrt{2}}[(c_1|\chi_1\rangle + c_2|\chi_2\rangle)\,(c_3|\mathrm{s}_1\tfrac{1}{2}\rangle + c_4|\mathrm{s}_1-\tfrac{1}{2}\rangle) - (-c_2|\chi_1\rangle + c_1|\chi_2\rangle)\,(-c_4|\mathrm{s}_1\tfrac{1}{2}\rangle + c_3|\mathrm{s}_1-\tfrac{1}{2}\rangle)\\
&\times \tfrac{1}{\sqrt{2}}[(c_1|\chi_3\rangle - c_2|\chi_4\rangle)\,(c_3|\mathrm{s}_2\tfrac{1}{2}\rangle - c_4|\mathrm{s}_2-\tfrac{1}{2}\rangle) - (c_2|\chi_3\rangle + c_1|\chi_4\rangle)\,(c_4|\mathrm{s}_2\tfrac{1}{2}\rangle + c_3|\mathrm{s}_2-\tfrac{1}{2}\rangle)]\},
\end{aligned} \tag{4.12}$$

with

$$c_1^2+c_2^2 = c_3^2+c_4^2 = 1. \tag{4.13}$$

Both the coefficients c_1–c_4 appearing in the wavefunction (4.12) and the H_1EH_2 bond angle upon which they depend are determined by the condition that the total energy, composed of the purely electronic energy $\langle\psi_{\kappa\mathrm{v}}|\mathscr{H}_{\mathrm{Br}}|\psi_{\kappa\mathrm{v}}\rangle$ plus the internuclear repulsion (E_{nuc}), be a minimum. This condition is entirely equivalent to minimizing the interaction energy ($\langle\psi_{\kappa\mathrm{v}}|\mathscr{H}_{\mathrm{Br}}|\psi_{\kappa\mathrm{v}}\rangle + E_{\mathrm{nuc}} - E_{\mathrm{E}} - 2E_{\mathrm{H}}$), where E_{E} is the energy of the $J = 2$ ground level of the p² configuration of the heavy element. When the interaction energy is calculated by using the methods of §3 (*a*), it is found to contain the two terms

$$\begin{aligned}
I_1 = -&\langle(c_1\chi_1 + c_2\chi_2)|(c_3\mathrm{s}_1\tfrac{1}{2} + c_4\mathrm{s}_1-\tfrac{1}{2})\rangle\\
&\times\langle(c_3\mathrm{s}_1\tfrac{1}{2} + c_4\mathrm{s}_1-\tfrac{1}{2})|\hat{V}_{\mathrm{NE}} + \hat{V}_{\mathrm{CDF}} + \hat{V}_{1,\mathrm{H}}|(c_1\chi_1 + c_2\chi_2)\rangle,
\end{aligned} \tag{4.14a}$$

$$\begin{aligned}
I_2 = &\langle(c_1\chi_1 + c_2\chi_2)|(-c_4\mathrm{s}_1\tfrac{1}{2} + c_3\mathrm{s}_1-\tfrac{1}{2})\rangle\\
&\times\langle(c_3\mathrm{s}_1\tfrac{1}{2} + c_4\mathrm{s}_1-\tfrac{1}{2})|\hat{V}_{\mathrm{NE}} + \hat{V}_{\mathrm{CDF}} + \hat{V}_{1,\mathrm{H}}|(-c_2\chi_1 + c_1\chi_2)\rangle.
\end{aligned} \tag{4.14b}$$

where $\hat{V}_{\mathrm{CDF}}$ is the Dirac–Fock potential due to the core of the heavy element and $\hat{V}_{1,\mathrm{H}}$ is that due to proton 1. The quantity I_1 is the exact analogue of the term in $\eta\langle \mathrm{s}^{\mathrm{NR}}|\mathrm{p}^{\mathrm{NR}}\rangle$ in the interaction energy $E_{\mathrm{int}}({}^3\Sigma)$, (3.12*a*), responsible for the repulsion predicted by the non-orthogonal Heitler–London triplet wavefunction $|{}^3\Sigma\rangle$, (3.11*a*). Both this term and I_1 are easily seen to be positive. The quantity I_2 (4.14*b*), being analogous to the attractive overlap term responsible for a large fraction of the bonding displayed in the Kappa-valence method by a p–H bond, is likely to be an important contributer to the energy of the t_1–H_1 bond. Since the repulsive contribution I_1 vanishes if the overlap $\langle \mathrm{t}_1|(c_3\mathrm{s}_{1\frac{1}{2}}+c_4\mathrm{s}_{1-\frac{1}{2}})\rangle$ is zero while the attractive term I_2 is proportional to the overlap $\langle \mathrm{t}_1|(-c_4\mathrm{s}_{1\frac{1}{2}}+c_3\mathrm{s}_{1-\frac{1}{2}})\rangle$, it follows that the interaction energy predicted by (4.12) can be approximately minimized by demanding that

$$\langle \mathrm{t}_1|(c_3\mathrm{s}_{1\frac{1}{2}}+c_4\mathrm{s}_{1-\frac{1}{2}})\rangle = 0, \tag{4.15}$$

while maximizing

$$F = \langle \mathrm{t}_1|(-c_4\mathrm{s}_{1\frac{1}{2}}+c_3\mathrm{s}_{1-\frac{1}{2}})\rangle, \tag{4.16}$$

subject to (4.13). This approach can be expected to predict the bond angle quite well because the coulomb-type terms in the interaction energy will be relatively insensitive to this angle. This method also neglects the energy needed to excite the $J = 2$ ground state of the heavy element to the valence state, which is a mixture of the $J = 0$ and $J = 2$ levels of the ground p^2 manifold, that can be extracted from (4.12). This quantity will be small for E116, however, because even the $\mathrm{p}^2_2 \to \mathrm{p}^2_0$ excitation energy is predicted to be $10^4\ \mathrm{cm}^{-1}$ (paper I). The neglect of the inter-proton repulsion implicit in determining the wavefunction solely through the two conditions (4.15) and (4.16) is likely to be a good approximation because it is known from non-relativistic valence theory that molecular geometry is largely determined by electronic factors. One good example of this is provided by the bond angles in $\mathrm{H_2S}$, $\mathrm{H_2Se}$ and $\mathrm{H_2Te}$ whose electronic structures can be described as consisting of bonds to two pure p orbitals on the central atom.

It is shown in appendix 5 that, for any given geometry, the wavefunction (4.12) is still not completely determined by the conditions (4.15) and (4.16) so that the further orthogonality condition

$$\langle \mathrm{t}_1|(c_3\mathrm{s}_{2\frac{1}{2}}-c_4\mathrm{s}_{2-\frac{1}{2}})\rangle = 0, \tag{4.17}$$

can be usefully imposed. It is further shown (appendix 5) by maximizing the quantity (4.16) that the equilibrium bond angle is predicted to be 90° for which geometry the coefficients c_i (4.12) are $c_1 = \frac{\sqrt{3}}{2}$, $c_2 = \frac{1}{2}$ and $c_3 = c_4 = \frac{1}{\sqrt{2}}$. This shows through (4.11) that at the equilibrium bond angle the four hybrids are

$$\left.\begin{aligned}
|\mathrm{t}_1\rangle &= \tfrac{1}{2\sqrt{2}}[\sqrt{3}(|\mathrm{p}_{\frac{1}{2}}\rangle-|\mathrm{p}_{\frac{3}{2}}\rangle)-|\mathrm{p}_{-\frac{1}{2}}\rangle-|\mathrm{p}_{-\frac{3}{2}}\rangle],\\
|\mathrm{t}_2\rangle &= \tfrac{1}{2\sqrt{2}}[-|\mathrm{p}_{\frac{1}{2}}\rangle+|\mathrm{p}_{\frac{3}{2}}\rangle-\sqrt{3}(|\mathrm{p}_{-\frac{1}{2}}\rangle+|\mathrm{p}_{-\frac{3}{2}}\rangle)],\\
|\mathrm{t}_3\rangle &= \tfrac{1}{2\sqrt{2}}[-\sqrt{3}(|\mathrm{p}_{\frac{1}{2}}\rangle+|\mathrm{p}_{\frac{3}{2}}\rangle)-|\mathrm{p}_{-\frac{1}{2}}\rangle+|\mathrm{p}_{-\frac{3}{2}}\rangle],\\
|\mathrm{t}_4\rangle &= \tfrac{1}{2\sqrt{2}}[-|\mathrm{p}_{\frac{1}{2}}\rangle-|\mathrm{p}_{\frac{3}{2}}\rangle+\sqrt{3}(|\mathrm{p}_{-\frac{1}{2}}\rangle-|\mathrm{p}_{-\frac{3}{2}}\rangle)].
\end{aligned}\right\} \tag{4.18}$$

Use of the results (3.9) shows, after expressing the $\mathrm{p}_{\pm1}$ as $\mathrm{p}_{\pm1} = \mp\frac{1}{\sqrt{2}}(\mathrm{p}_x-\mathrm{i}\mathrm{p}_y)$, that the large components of the hybrids (4.18) are

$$\left.\begin{aligned}
|\mathrm{t}_1\rangle_{\mathrm{L}} &= \tfrac{1}{2}[|(\mathrm{p}_z+\tfrac{1}{\sqrt{3}}\mathrm{p}_x)\,\alpha\rangle-|(\mathrm{p}_x+\tfrac{1}{\sqrt{3}}\mathrm{p}_z)\,\beta\rangle+\tfrac{2}{\sqrt{3}}\mathrm{i}|\mathrm{p}_y\,\alpha\rangle],\\
|\mathrm{t}_2\rangle_{\mathrm{L}} &= -\tfrac{1}{2}[|(\mathrm{p}_z+\tfrac{1}{\sqrt{3}}\mathrm{p}_x)\,\beta\rangle+|(\mathrm{p}_x+\tfrac{1}{\sqrt{3}}\mathrm{p}_z)\,\alpha\rangle-\tfrac{2}{\sqrt{3}}\mathrm{i}|\mathrm{p}_y\,\beta\rangle],\\
|\mathrm{t}_3\rangle_{\mathrm{L}} &= \tfrac{1}{2}[|(-\mathrm{p}_z+\tfrac{1}{\sqrt{3}}\mathrm{p}_x)\,\alpha\rangle+|(\mathrm{p}_x-\tfrac{1}{\sqrt{3}}\mathrm{p}_z)\,\beta\rangle+\tfrac{2}{\sqrt{3}}\mathrm{i}|\mathrm{p}_y\,\alpha\rangle],\\
|\mathrm{t}_4\rangle_{\mathrm{L}} &= -\tfrac{1}{2}[|(-\mathrm{p}_z+\tfrac{1}{\sqrt{3}}\mathrm{p}_x)\,\alpha\rangle-|(\mathrm{p}_x-\tfrac{1}{\sqrt{3}}\mathrm{p}_z)\,\alpha\rangle-\tfrac{2}{\sqrt{3}}\mathrm{i}|\mathrm{p}_y\,\beta\rangle].
\end{aligned}\right\} \tag{4.19}$$

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Since $\frac{1}{\sqrt{2}}(\mathrm{p}_x+\mathrm{p}_z)$ and $\frac{1}{\sqrt{2}}(\mathrm{p}_x-\mathrm{p}_z)$ are σ orbitals pointing along the E–H$_1$ and E–H$_2$ bonds respectively, the large components (4.19) are written more transparently as

$$\left.\begin{aligned}
|\mathrm{t}_1\rangle_{\mathrm{L}} &= \frac{1+\sqrt{3}}{2\sqrt{3}}\,|\tfrac{1}{\sqrt{2}}(\mathrm{p}_x+\mathrm{p}_z)\,\mathrm{x}_-\rangle-\frac{\sqrt{3}-1}{2\sqrt{3}}\,|\tfrac{1}{\sqrt{2}}(\mathrm{p}_x-\mathrm{p}_z)\,\mathrm{x}_+\rangle+\tfrac{1}{\sqrt{3}}\mathrm{i}|\mathrm{p}_y\,\tfrac{1}{\sqrt{2}}(\mathrm{x}_++\mathrm{x}_-)\rangle,\\
|\mathrm{t}_2\rangle_{\mathrm{L}} &= -\frac{1+\sqrt{3}}{2\sqrt{3}}\,|\tfrac{1}{\sqrt{2}}(\mathrm{p}_x+\mathrm{p}_z)\,\mathrm{x}_+\rangle-\frac{\sqrt{3}-1}{2\sqrt{3}}\,|\tfrac{1}{\sqrt{2}}(\mathrm{p}_x-\mathrm{p}_z)\,\mathrm{x}_-\rangle+\tfrac{1}{\sqrt{3}}\mathrm{i}|\mathrm{p}_y\,\tfrac{1}{\sqrt{2}}(\mathrm{x}_+-\mathrm{x}_-)\rangle,\\
|\mathrm{t}_3\rangle_{\mathrm{L}} &= \frac{1+\sqrt{3}}{2\sqrt{3}}\,|\tfrac{1}{\sqrt{2}}(\mathrm{p}_x-\mathrm{p}_z)\,\mathrm{x}_+\rangle-\frac{\sqrt{3}-1}{2\sqrt{3}}\,|\tfrac{1}{\sqrt{2}}(\mathrm{p}_x+\mathrm{p}_z)\,\mathrm{x}_-\rangle+\tfrac{1}{\sqrt{3}}\mathrm{i}|\mathrm{p}_y\,\tfrac{1}{\sqrt{2}}(\mathrm{x}_++\mathrm{x}_-)\rangle,\\
|\mathrm{t}_4\rangle_{\mathrm{L}} &= \frac{1+\sqrt{3}}{2\sqrt{3}}\,|\tfrac{1}{\sqrt{2}}(\mathrm{p}_x-\mathrm{p}_z)\,\mathrm{x}_-\rangle+\frac{\sqrt{3}-1}{2\sqrt{3}}\,|\tfrac{1}{\sqrt{2}}(\mathrm{p}_x+\mathrm{p}_z)\,\mathrm{x}_+\rangle+\tfrac{1}{\sqrt{3}}\mathrm{i}|\mathrm{p}_y\,\tfrac{1}{\sqrt{2}}(\mathrm{x}_+-\mathrm{x}_-)\rangle,
\end{aligned}\right\}\tag{4.20}$$

where $|\mathrm{x}+\rangle$ and $|\mathrm{x}-\rangle$ are the eigenfunctions of the Pauli spin operator $\hat{\mathrm{S}}_x$ defined by

$$|\mathrm{x}_+\rangle = \tfrac{1}{\sqrt{2}}(|\alpha\rangle+|\beta\rangle),\quad |\mathrm{x}_-\rangle = \tfrac{1}{\sqrt{2}}(|\alpha\rangle-|\beta\rangle).\tag{4.21}$$

The large components of the valence part of the wavefunction (4.12) are, when expressed in terms of the hybrids (4.20), given by

$$\begin{aligned}
|\psi_{\kappa\mathrm{v}}(\mathrm{val})\rangle_{\mathrm{L}} = S\hat{\mathscr{A}}\Bigg[\Bigg\{&\frac{1+\sqrt{3}}{2\sqrt{3}}\,[|\tfrac{1}{\sqrt{2}}(\mathrm{p}_x+\mathrm{p}_z)\,\mathrm{s}_1\rangle\,\tfrac{1}{\sqrt{2}}|\mathrm{x}_-\mathrm{x}_+-\mathrm{x}_+\mathrm{x}_-\rangle]\\
&-\frac{\sqrt{3}-1}{2\sqrt{3}}\,[|\tfrac{1}{\sqrt{2}}(\mathrm{p}_x-\mathrm{p}_z)\,\mathrm{s}_1\rangle\,\tfrac{1}{\sqrt{2}}|\mathrm{x}_+\mathrm{x}_++\mathrm{x}_-\mathrm{x}_-\rangle]\\
&+\tfrac{1}{\sqrt{3}}\mathrm{i}[|\mathrm{p}_y\mathrm{s}_1\rangle\,\tfrac{1}{\sqrt{2}}(\tfrac{1}{\sqrt{2}}|\mathrm{x}_+\mathrm{x}_+-\mathrm{x}_-\mathrm{x}_-\rangle+\tfrac{1}{\sqrt{2}}|\mathrm{x}_+\mathrm{x}_-+\mathrm{x}_-\mathrm{x}_+\rangle)]\Bigg\}\\
\times\Bigg\{&\frac{1+\sqrt{3}}{2\sqrt{3}}\,[|\tfrac{1}{\sqrt{2}}(\mathrm{p}_x-\mathrm{p}_z)\,\mathrm{s}_2\rangle\,\tfrac{1}{\sqrt{2}}|\mathrm{x}_+\mathrm{x}_--\mathrm{x}_-\mathrm{x}_+\rangle]\\
&-\frac{\sqrt{3}-1}{2\sqrt{3}}\,[|\tfrac{1}{\sqrt{2}}(\mathrm{p}_x+\mathrm{p}_z)\,\mathrm{s}_2\rangle\,\tfrac{1}{\sqrt{2}}|\mathrm{x}_+\mathrm{x}_++\mathrm{x}_-\mathrm{x}_-\rangle]\\
&+\tfrac{1}{\sqrt{3}}\mathrm{i}[|\mathrm{p}_y\mathrm{s}_2\rangle\,\tfrac{1}{\sqrt{2}}(\tfrac{1}{\sqrt{2}}|\mathrm{x}_-\mathrm{x}_--\mathrm{x}_+\mathrm{x}_+\rangle+\tfrac{1}{\sqrt{2}}|\mathrm{x}_+\mathrm{x}_-+\mathrm{x}_-\mathrm{x}_+\rangle)]\Bigg\}\Bigg],
\end{aligned}\tag{4.22}$$

where s_1 and s_2 are the spatial 1s orbitals on the hydrogen atoms 1 and 2 respectively.

The nature of the bonding in the dihydride can be deduced by examining the large components of the valence part of the wavefunction because these essentially determine the interaction energy as discussed in §3. It should be noted that the orbital $\frac{1}{\sqrt{2}}(\mathrm{p}_x-\mathrm{p}_z)$ bears the same spatial relation to the 1s orbital on proton 1 as the π symmetry term in the large components of the orbitals $|\mathrm{v}\rangle$ bears towards the hydrogen s orbital in a p–H bond, (3.1). Thus both the overlaps $\langle\mathrm{s}_1|\frac{1}{\sqrt{2}}(\mathrm{p}_x-\mathrm{p}_z)\rangle$ and $\langle\mathrm{s}_2|\frac{1}{\sqrt{2}}(\mathrm{p}_x+\mathrm{p}_z)\rangle$ vanish at the predicted bond angle of 90°. The large components (4.22) thus show that each bond consists of one term of the non-orthogonal Heitler–London singlet type plus five terms of the orthogonal triplet type. The non-orthogonal Heitler–London singlet component in each bond is slightly less ($[(1+\sqrt{3})/2\sqrt{3}]^2 = 0.6220$) than that ($\frac{2}{3}$) in the p–H bond (3.1). Consequently, with the order of an orthogonal triplet bond taken to be one half as discussed previously (Pyper 1980*a*) each of the bonds in (4.22) is predicted to have an order of 0.811 rather than $\frac{5}{6}$ as predicted for a p–H bond (3.1). This description cannot be regarded as entirely complete, however, because it neglects the interaction between the bonds. Although imposition of the condition (4.17) reduces this interaction, it is still not entirely absent because the large components of $|\mathrm{t}_1\rangle$ and $|\mathrm{t}_4\rangle$ overlap with $|\mathrm{s}_2\mathrm{x}_+\rangle$

and $|s_1 x_+\rangle$ respectively, which are functions involving the hydrogen atom to which the hybrid is not bonded. The overlaps $\langle s_2 x_- | t_2\rangle_L$ and $\langle s_1 x_- | t_3\rangle_L$ are similarly non-zero. These non-vanishing overlaps give rise to two repulsive terms of the same form as the exchange contribution (involving $\hat{P}_{12}$ in (3.3)) to the interaction energy $E_{\text{int}}(^3\Sigma)$ predicted by a non-orthogonal Heitler–London triplet wavefunction, (3.11*a*). The coefficient multiplying these two terms is $\frac{1}{12}(\sqrt{3}-1)^2$ $(= 0.045)$ which suggests that the overall order of each p–H bond in (4.22) and hence (4.12) should be taken to be 0.766 (= 0.811–0.045) rather than 0.811. Although analogous destabilizing interactions arise in non-relativistic valence theory, it appears that they are less unimportant in the present relativistic problem. Thus although both the sp and sp^2 hybrids, used to describe the electronic structure of BeH_2 and CH_3 respectively, overlap with the hydrogen orbitals to which they are not bonded, these overlaps consist of two distinct spatial integrals which enter with opposite signs. For example in BeH_2, the overlap between s_2 and the hybrid $\frac{1}{\sqrt{2}}(2s+2p_z)$ which is bonded to hydrogen atom one is $\frac{1}{\sqrt{2}}(\langle s_2|2s\rangle - \langle s_1|2p_z\rangle)$, where both $\langle s_2|2s\rangle$ and $\langle s_1|2p_z\rangle$ are positive. Clearly there is an internuclear separation for which this overlap vanishes. However there is no corresponding cancellation in the overlaps of the type $\langle s_2 x_+ | t_1\rangle_L$ responsible for the destabilizing interaction of the two bonds in (4.22) and (4.12).

Evidence that the methods used here to investigate the bonding in H–E–H are not unreasonable is provided by applying them to the corresponding non-relativistic problem. Since the p_y orbital clearly plays no role in the bonding, the expression (4.6*a*) for the hybrids forming the bonds becomes

$$|t_1\rangle = d_1|p_z\,\alpha\rangle + d_2|p_x\,\alpha\rangle + d_3|p_z\,\beta\rangle + d_4|p_x\,\beta\rangle. \tag{4.23}$$

The three further hybrids $|t_2\rangle$, $|t_3\rangle$ and $|t_4\rangle$ are defined from (4.23) by relations identical to (4.1) except that the 4×4 matrix Σ_q used to define $\hat{H}_{q,\,t}$, (2.12), is replaced by the 2×2 matrix σ_q^p. The conditions (4.9) and (4.10) then show that $d_1 = \pm d_2$ and $d_3 = \pm d_4$. It is again found that the wavefunction is not uniquely defined by (4.15) and the condition of maximum overlap, and hence that the further condition (4.17) must be imposed. It is again found that the bond angle, predicted by maximizing the overlap, is 90° and hence, through an equation of the type (A 5.11), that the valence part of the wavefunction is

$$|\psi_{\kappa\mathrm{V}}^{\mathrm{NR}}(\mathrm{val})\rangle = S\hat{\mathscr{A}}\{[|\tfrac{1}{\sqrt{2}}(p_x+p_z)\,s_1\rangle\,\tfrac{1}{\sqrt{2}}|\alpha\beta-\beta\alpha\rangle]\,[|\tfrac{1}{\sqrt{2}}(p_x-p_z)\,s_2\rangle\,\tfrac{1}{\sqrt{2}}|\alpha\beta-\beta\alpha\rangle]\}. \tag{4.24}$$

This consists of two essentially independent Heitler–London non-orthogonal singlet covalent bonds, each one being formed between one of the hydrogen 1s orbitals and a pure p_σ orbital directed exactly along the bond. It would have been impossible to have had any confidence in the predictions for the relativistic problem if this result, which is a standard part of non-relativistic valence theory, had not been obtained.

It has been shown, by constructing a wavefunction consisting of two Kappa-valence bonds of the type (4.1), that the ground manifold of a heavy element having two electrons occupying a Dirac–Fock p orbital can bond two groups each of which is described non-relativistically as having an unpaired electron in a σ orbital. Each of the bonds is predicted to be slightly weaker, having an order of 0.77, than the bond, whose order is $\frac{5}{6}$, formed between such a group and the ground state of a heavy element having a single valence σ electron. The bond angle in these divalent compounds is predicted to be close to 90°. It should be pointed out that these conclusions do not necessarily apply if the bonded groups have valence π electrons.

(*b*) *The relativistic molecular orbital description of* p^2 *dihydrides*

(i) *The linear geometry*

The high symmetry of the linear molecule enables the relativistic molecular orbitals for this geometry to be calculated readily. However, it does not appear to be possible to calculate the molecular orbitals for a bent H–E–H molecule simply without either making the Huckel-type approximation of neglecting overlap or using some of the results of the Kappa valence method. Nevertheless it can be shown without recourse to either of these two approaches that relativistic molecular orbital theory unambiguously predicts that an H–E–H molecule in which the heavy element (E) remains in its ground p^2 manifold will be bent. This prediction can be made because the readily calculated molecular orbitals for the linear molecule can be used to construct a Walsh-type diagram (Walsh 1953) valid for small angles of bend.

It was shown in §2 that relativistic molecular orbitals for linear AB$_2$ molecules are eigenfunctions of $\hat{\mathrm{J}}_z$, $\hat{\mathrm{H}}_{z,\mathrm{t}}$ and $\hat{\mathrm{I}}_\mathrm{t}$. The relations (2.31) and (4.4) show that, out of the eight symmetrized basis functions that can be constructed from the four p orbitals and the four hydrogen orbitals, the four functions $|\mathrm{p}\tfrac{3}{2}\rangle$, $|\mathrm{p}-\tfrac{1}{2}\rangle$, $\tfrac{1}{\sqrt{2}}(|\mathrm{s}_1-\tfrac{1}{2}\rangle-|\mathrm{s}_2-\tfrac{1}{2}\rangle)$ and $\tfrac{1}{\sqrt{2}}(|\mathrm{s}_1\tfrac{1}{2}\rangle+|\mathrm{s}_2\tfrac{1}{2}\rangle)$ are eigenfunctions of $\hat{\mathrm{H}}_{z,\mathrm{t}}$ of eigenvalue i while the functions $|\mathrm{p}-\tfrac{3}{2}\rangle$, $|\mathrm{p}\tfrac{1}{2}\rangle$, $\tfrac{1}{\sqrt{2}}(|\mathrm{s}_1\tfrac{1}{2}\rangle-|\mathrm{s}_2\tfrac{1}{2}\rangle)$ and $\tfrac{1}{\sqrt{2}}(|\mathrm{s}_1-\tfrac{1}{2}\rangle+|\mathrm{s}_2-\tfrac{1}{2}\rangle)$ are eigenfunctions of $\hat{\mathrm{H}}_{z,\mathrm{t}}$ of eigenvalue $-$i. If the atomic orbitals $|\chi_\mathrm{t} m\rangle$ in the expansion (3.28) for the molecular orbitals are replaced by symmetry-adapted functions, there are no non-zero off-diagonal matrix elements of the molecular Fock operator between any one of the four symmetry-adapted functions having $\hat{\mathrm{H}}_{z,\mathrm{t}}$-eigenvalue i and any one of the four functions having eigenvalue of $\hat{\mathrm{H}}_{z,\mathrm{t}}$ $-$i. It follows from this result, the vanishing of all the Fock matrix elements between pairs of functions differing in the m_j quantum number, and the assumption that the Fock matrix elements $\langle \mathrm{p}m|\hat{\mathrm{F}}_\mathrm{M}|\mathrm{p}m\rangle$ and $\langle \mathrm{s}_1 m|\hat{\mathrm{F}}_\mathrm{M}|\mathrm{s}_1 m\rangle$ are equal, which is consistent with the postulate of purely covalent bonding, that the relativistic molecular orbitals for the linear geometry are

$$\left.\begin{aligned}
|\phi_1-\tfrac{1}{2}-1\mathrm{i}\rangle &= \tfrac{1}{\sqrt{2}}S_1[|\mathrm{p}-\tfrac{1}{2}\rangle+\tfrac{1}{\sqrt{2}}(|\mathrm{s}_1-\tfrac{1}{2}\rangle-|\mathrm{s}_2-\tfrac{1}{2}\rangle)], & |\phi\tfrac{1}{2}1\mathrm{i}\rangle &= \tfrac{1}{\sqrt{2}}(|\mathrm{s}_1\tfrac{1}{2}\rangle+|\mathrm{s}_2\tfrac{1}{2}\rangle),\\
|\phi_2-\tfrac{1}{2}-1\mathrm{i}\rangle &= \tfrac{1}{\sqrt{2}}S_2[|\mathrm{p}-\tfrac{1}{2}\rangle-\tfrac{1}{\sqrt{2}}(|\mathrm{s}_1-\tfrac{1}{2}\rangle-|\mathrm{s}_2-\tfrac{1}{2}\rangle)], & |\phi\tfrac{3}{2}-1\mathrm{i}\rangle &= |\mathrm{p}\tfrac{3}{2}\rangle,\\
|\phi_1\tfrac{1}{2}-1-\mathrm{i}\rangle &= \tfrac{1}{\sqrt{2}}S_1[|\mathrm{p}\tfrac{1}{2}\rangle+\tfrac{1}{\sqrt{2}}(|\mathrm{s}_1\tfrac{1}{2}\rangle-|\mathrm{s}_2\tfrac{1}{2}\rangle)], & |\phi-\tfrac{1}{2}1-\mathrm{i}\rangle &= \tfrac{1}{\sqrt{2}}(|\mathrm{s}_1-\tfrac{1}{2}\rangle+|\mathrm{s}_2-\tfrac{1}{2}\rangle),\\
|\phi_2\tfrac{1}{2}-1-\mathrm{i}\rangle &= \tfrac{1}{\sqrt{2}}S_2[|\mathrm{p}\tfrac{1}{2}\rangle-\tfrac{1}{\sqrt{2}}(|\mathrm{s}_1\tfrac{1}{2}\rangle-|\mathrm{s}_2\tfrac{1}{2}\rangle)], & |\phi-\tfrac{3}{2}-1-\mathrm{i}\rangle &= |\mathrm{p}-\tfrac{3}{2}\rangle.
\end{aligned}\right\}\quad(4.25)$$

Here the notation of §2 is used and S_1 and S_2 are normalization constants which become unity in the limit that the overlaps $\langle \mathrm{p}\tfrac{1}{2}|\mathrm{s}_\mu\tfrac{1}{2}\rangle$ are negligible. The result (2.18) shows that the orbitals $|\phi_a m i_\mathrm{p}\mathrm{i}\rangle$ and $|\phi_a - m i_\mathrm{p} - \mathrm{i}\rangle$ are degenerate. There are two bonding, ($|\phi_1-\tfrac{1}{2}-1\mathrm{i}\rangle$ and $|\phi_1\tfrac{1}{2}-1-\mathrm{i}\rangle$), and two anti-bonding, ($|\phi_2-\tfrac{1}{2}-1\mathrm{i}\rangle$ and $|\phi_2\tfrac{1}{2}-1-\mathrm{i}\rangle$), orbitals, the four remaining orbitals being non-bonding. Two of the four valence electrons are accommodated in the bonding orbitals leaving the two remaining electrons to enter non-bonding orbitals. Each of the bonding orbitals is the relativistic equivalent of a non-relativistic three-centre bonding molecular orbital. The arguments used in §3(*c*) to investigate the molecular orbital description of p–H bonds show that the bonds formed by occupation of these relativistic molecular orbitals are weaker than those resulting from occupation of a non-relativistic three-centre bonding orbital because the large components of $|\phi_1-\tfrac{1}{2}-1\mathrm{i}\rangle$ are

$$|\phi_1-\tfrac{1}{2}-1\mathrm{i}\rangle_\mathrm{L}=(1-\tfrac{1}{6}S_1^2)^{\frac{1}{2}}\{(1+\tfrac{4\sqrt{3}}{5}\langle \mathrm{s}_1|\mathrm{p}_z\rangle)^{-\frac{1}{2}}|\tfrac{1}{\sqrt{5}}[\sqrt{2}\mathrm{p}_z+\sqrt{\tfrac{3}{2}}(\mathrm{s}_1-\mathrm{s}_2)]\,\beta\rangle\}+\tfrac{1}{\sqrt{6}}S_1\,|\mathrm{p}_{-1}\alpha\rangle. \quad (4.26)$$

In the derivation of this result the normalization constant S_1 was expressed in terms of the large components. Since the fraction $\frac{1}{6}S_1^2$ of the density derived from (4.26) does not contribute to the overlap density responsible in molecular orbital theory for binding the protons, the result (4.26) predicts that the bonds in the linear molecule will be weaker than a non-relativistic three-centre two-electron bond which is itself significantly weaker than a normal covalent single bond.

For nonlinear geometries, the molecular orbitals cease to be eigenfunctions of $\hat{\mathrm{j}}_z$ and $\hat{\mathrm{I}}_{\mathrm{t}}$ although they are still eigenfunctions of $\hat{\mathrm{H}}_{z,\mathrm{t}}$. Hence the off-diagonal Fock matrix elements between any two orbitals having the same $\hat{\mathrm{H}}_{z,\mathrm{t}}$-eigenvalue will be non-zero and consequently the molecular orbitals for the bent molecule will be linear combinations of the functions (4.25). For small displacements from the linear geometry, the most important mixings are those within the two pairs of orbitals $|\phi\frac{1}{2}1\mathrm{i}\rangle$ plus $|\phi\frac{3}{2}-1\mathrm{i}\rangle$ and $|\phi-\frac{1}{2}1-\mathrm{i}\rangle$ plus $|\phi-\frac{3}{2}-1-\mathrm{i}\rangle$ because these pairs are degenerate for the linear geometry. Both of these orbital mixings produce two new orbitals, one of lower and one of higher energy, the previously non-bonding electrons occupying the two orbitals whose energies have been decreased which therefore acquire some bonding character. These arguments of the type originated by Walsh (1953) therefore show that relativistic molecular orbital theory predicts that H–E–H molecules will be bent.

(ii) *The nonlinear geometry*

For the bent molecule, there are four relativistic molecular orbitals denoted $|\phi_a\mathrm{i}\rangle$ in the notation of §2(*c*) which are eigenfunctions of $\hat{\mathrm{H}}_{z,\mathrm{t}}$ with eigenvalue i, that can be constructed from the valence p orbitals of the heavy element and the hydrogen orbitals. The remaining four valence molecular orbitals denoted $|\phi_a-\mathrm{i}\rangle$ $(a = 1, \ldots, 4)$ which are eigenfunctions of $\hat{\mathrm{H}}_{z,\mathrm{t}}$ of eigenvalue $-\mathrm{i}$ do not need to be considered in detail because it has been shown in §2(*b*) that each of these is degenerate with the molecular orbital $|\phi_a\mathrm{i}\rangle$ from which it can be generated by using (2.18) with $q = y$.

The four molecular orbitals $|\phi_a\mathrm{i}\rangle$ can be calculated by expanding them according to (3.28) replacing the Dirac–Fock atomic orbital basis $|\chi_t\rangle$ by the four symmetry-adapted combinations

$$|\mathrm{p}\tfrac{3}{2}\rangle,\ |\mathrm{p}-\tfrac{1}{2}\rangle,\ \tfrac{1}{\sqrt{2}}\,(|\mathrm{s}_1\tfrac{1}{2}\rangle+|\mathrm{s}_2\tfrac{1}{2}\rangle) \quad \text{and} \quad \tfrac{1}{\sqrt{2}}\,(|\mathrm{s}_1-\tfrac{1}{2}\rangle-|\mathrm{s}_2-\tfrac{1}{2}\rangle).$$

The molecular Fock hamiltonian $\hat{\mathrm{F}}_{\mathrm{M}}$ can be expressed as

$$\hat{\mathrm{F}}_{\mathrm{M}} = \mathscr{H}_{\mathrm{k.e.}}+\hat{V}_{\mathrm{H}_1}+\hat{V}_{\mathrm{H}_2}+\hat{V}_{\mathrm{CDFE}}+\hat{V}_{\mathrm{val}},$$

where $\hat{V}_{\mathrm{H}_1}$ and $\hat{V}_{\mathrm{H}_2}$ are the potentials due to the protons of the hydrogen atoms 1 and 2 respectively, $\hat{V}_{\mathrm{CDFE}}$ is the total coulomb plus exchange potential due to the core of the heavy element and $\hat{V}_{\mathrm{val}}$ is the sum of the coulomb and exchange potentials generated by the four valence electrons. Invoking the atomic Dirac equation (3.7*b*) satisfied by the hydrogen orbitals shows that the Fock matrix elements $\langle \mathrm{p}m|\hat{\mathrm{F}}_{\mathrm{M}}|\frac{1}{\sqrt{2}}(\mathrm{s}_1m'\pm\mathrm{s}_2m')\rangle$ can be expressed as

$$\langle \mathrm{p}m|\hat{\mathrm{F}}_{\mathrm{M}}|\tfrac{1}{\sqrt{2}}(\mathrm{s}_1m'\pm\mathrm{s}_2m')\rangle = \sqrt{2}(E_{\mathrm{H}}\langle \mathrm{p}m|\mathrm{s}_1m'\rangle+\langle \mathrm{p}m|\hat{V}_{\mathrm{H}_2}|\mathrm{s}_1m'\rangle+\langle \mathrm{p}m|\hat{V}_{\mathrm{CDFE}}+\hat{V}_{\mathrm{val}}|\mathrm{s}_1m'\rangle). \quad (4.27)$$

In (4.27) the identity $\langle \mathrm{p}m|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{s}_1m'\rangle = \langle \mathrm{p}m|\hat{\mathrm{H}}_{z,\mathrm{t}}^{-1}\hat{\mathrm{F}}_{\mathrm{M}}\hat{\mathrm{H}}_{z,\mathrm{t}}|\mathrm{s}_1m'\rangle$ and the relations (2.31) have been used to relate the matrix element $\langle \mathrm{p}m|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{s}_1m'\rangle$ to $\langle \mathrm{p}m|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{s}_2m'\rangle$. Since the expression (4.27) contains no terms linking the large and small components, these matrix elements can be approximated by just the terms involving the large components because these will be greater by a factor of c^2 than those involving the small components. The qualitative features of the bonding will be revealed by both neglecting the three-centre integrals $\langle \mathrm{p}m|\hat{V}_{\mathrm{H}_2}|\mathrm{s}_1 m'\rangle$ which will be small and by taking the quantities $\langle \mathrm{p}m|\hat{V}_{\mathrm{CDFE}}+\hat{V}_{\mathrm{val}}|\mathrm{s}_1 m'\rangle$ to be proportional to the overlap integrals $\langle \mathrm{p}m|\mathrm{s}_1 m'\rangle$. With the further assumption that the bond lengths are independent of the bond angle, it follows that the matrix elements arising in the evaluation of (4.27) between the spinless one-component functions p_x, p_z and s_1 can be expressed as

$$E_{\mathrm{H}}\langle \mathrm{p}_x|\mathrm{s}_1\rangle + \langle \mathrm{p}_x|\hat{V}'_{\mathrm{CDFE}}+\hat{V}'_{\mathrm{val}}|\mathrm{s}_1\rangle = F\sin\alpha, \tag{4.28a}$$

$$E_{\mathrm{H}}\langle \mathrm{p}_z|\mathrm{s}_1\rangle + \langle \mathrm{p}_z|\hat{V}'_{\mathrm{CDFE}}+\hat{V}_{\mathrm{val}}|\mathrm{s}_1\rangle = F\cos\alpha, \tag{4.28b}$$

where F is the value of the quantity (4.28 *b*) for the linear geometry ($\alpha = 0$). Evaluation by these methods of the matrix elements of the molecular Fock operator between the four symmetrized basis functions having eigenvalue i of $\hat{\mathrm{H}}_{z,\mathrm{t}}$ shows, with the use of (4.27), the large components (3.9) and (4.28), that this part ($\boldsymbol{F}_{\mathrm{Mi}}$) of the Fock matrix $\boldsymbol{F}_{\mathrm{M}}$ (3.29) is

$$\begin{array}{cc} & \begin{array}{cccc} |\mathrm{p}\tfrac{3}{2}\rangle & |\mathrm{p}-\tfrac{1}{2}\rangle & \tfrac{1}{\sqrt{2}}(|\mathrm{s}_1\tfrac{1}{2}\rangle+|\mathrm{s}_2\tfrac{1}{2}\rangle) & \tfrac{1}{\sqrt{2}}(|\mathrm{s}_1-\tfrac{1}{2}\rangle-|\mathrm{s}_2-\tfrac{1}{2}\rangle) \end{array} \\ \boldsymbol{F}_{\mathrm{Mi}} = & \left[\begin{array}{cccc} d & 0 & -F\sin\alpha & 0 \\ 0 & d & \tfrac{1}{\sqrt{3}}F\sin\alpha & \tfrac{2}{\sqrt{3}}F\cos\alpha \\ -F\sin\alpha & \tfrac{1}{\sqrt{3}}F\sin\alpha & d & 0 \\ 0 & \tfrac{2}{\sqrt{3}}F\cos\alpha & 0 & d \end{array}\right], \end{array} \tag{4.29}$$

where the diagonal elements have been taken to be equal to ensure consistency with the idea that the bonding is purely covalent. In the same approximation used to calculate the matrix elements $\langle \mathrm{p}m|\hat{\mathrm{F}}_{\mathrm{M}}|\tfrac{1}{\sqrt{2}}(\mathrm{s}_1 m' \pm \mathrm{s}_2 m')\rangle$, the two elements $\langle \mathrm{p}\tfrac{3}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}-\tfrac{1}{2}\rangle$ and $\langle \tfrac{1}{\sqrt{2}}(\mathrm{s}_1\tfrac{1}{2}+\mathrm{s}_2\tfrac{1}{2})|\hat{\mathrm{F}}_{\mathrm{M}} |\tfrac{1}{\sqrt{2}}(\mathrm{s}_1-\tfrac{1}{2}-\mathrm{s}_2-\tfrac{1}{2})\rangle$ vanish. Use of the Huckel-type approximation of replacing the overlap matrix in (3.29) by the unit matrix enables these equations with $\boldsymbol{F}_{\mathrm{M}}$ given by (4.29) to be solved analytically to yield the two bonding orbitals $|\phi_1 \mathrm{i}\rangle$ and $|\phi_2 \mathrm{i}\rangle$ of energies ϵ_1 and ϵ_2 given by

$$\left.\begin{aligned} \epsilon_1 &= d+\sqrt{\tfrac{2}{3}}F[1+(1-3\cos^2\alpha\sin^2\alpha)^{\frac{1}{2}}]^{\frac{1}{2}} \equiv d+b_1, \\ \epsilon_2 &= d+\sqrt{\tfrac{2}{3}}F[1-(1-3\cos^2\alpha\sin^2\alpha)^{\frac{1}{2}}]^{\frac{1}{2}} \equiv d+b_2. \end{aligned}\right\} \tag{4.30}$$

The two remaining orbitals $|\phi_3 \mathrm{i}\rangle$ and $|\phi_4 \mathrm{i}\rangle$ of respective energies $d-b_1$ and $d-b_2$ are the antibonding equivalents of $|\phi_1 \mathrm{i}\rangle$ and $|\phi_2 \mathrm{i}\rangle$. The results (4.30) show that both the orbital energies and the coefficients c_{ti} (3.28) depend on the molecular geometry. It is not possible in any simple way to determine the equilibrium bond angle by minimizing the total energy of the N-electron relativistic molecular orbital wavefunction. However, the success of Walsh diagrams (Walsh 1953) in explaining molecular geometries indicates that the orbital energies or some quantities closely related to them play an important role in determining the geometry even though the theoretical basis of Walsh diagrams is not absolutely clear (Buenker & Peyerimhoff 1974, Ferguson & Pyper 1980). This observation suggests that the equilibrium bond angle can be determined by minimizing the sum ($\epsilon_1+\epsilon_2$) of the energies of the bonding orbitals that are occupied. This procedure yields the same prediction as the Kappa-valence method that the equilibrium bond angle is 90° for which geometry the bonding molecular orbitals are found from (3.29) to be

$$|\phi_1 \mathrm{i}\rangle = \tfrac{1}{2\sqrt{2}}(-|\mathrm{p}\tfrac{3}{2}\rangle+\sqrt{3}|\mathrm{p}-\tfrac{1}{2}\rangle+|\mathrm{s}_1\tfrac{1}{2}\rangle+|\mathrm{s}_2\tfrac{1}{2}\rangle+|\mathrm{s}_1-\tfrac{1}{2}\rangle-|\mathrm{s}_2-\tfrac{1}{2}\rangle), \tag{4.31a}$$

$$|\phi_2 \mathrm{i}\rangle = -\tfrac{1}{2\sqrt{2}}(\sqrt{3}|\mathrm{p}\tfrac{3}{2}\rangle+|\mathrm{p}-\tfrac{1}{2}\rangle-|\mathrm{s}_1\tfrac{1}{2}\rangle-|\mathrm{s}_2\tfrac{1}{2}\rangle+|\mathrm{s}_1-\tfrac{1}{2}\rangle-|\mathrm{s}_2-\tfrac{1}{2}\rangle). \tag{4.31b}$$

The energies ϵ_1 and ϵ_2 of these two molecular orbitals are $d+F$ and $d+\frac{1}{\sqrt{3}}F$ respectively. These energies are interpreted by realizing that F as defined by (4.28*b*) is just the resonance integral for a non-relativistic p_z–s bond in a diatomic molecule.

The discussion presented in §3(*c*ii) shows that the bonding properties of the molecular orbitals (4.31) can be investigated by examining their large components. Substitution of the large components (3.9) into both (4.31) and the expressions for the molecular orbitals $|\phi_1 - i\rangle$ and $|\phi_2 - i\rangle$ obtained by operating on (4.31) with $\hat{H}_{y,t}$ shows that the large components of the molecular orbitals are

$$\left.\begin{aligned}
|\phi_1 i\rangle_L &= \tfrac{1}{\sqrt{2}}|[\tfrac{1}{\sqrt{2}}p_z + \tfrac{1}{2}(s_1 - s_2)]\,\beta\rangle + \tfrac{1}{\sqrt{2}}|[\tfrac{1}{\sqrt{2}}p_x + \tfrac{1}{2}(s_1 + s_2)]\,\alpha\rangle,\\
|\phi_1 - i\rangle_L &= \tfrac{1}{\sqrt{2}}|[\tfrac{1}{\sqrt{2}}p_z + \tfrac{1}{2}(s_1 - s_2)]\,\alpha\rangle - \tfrac{1}{\sqrt{2}}|[\tfrac{1}{\sqrt{2}}p_x + \tfrac{1}{2}(s_1 + s_2)]\,\beta\rangle,\\
|\phi_2 i\rangle_L &= -\tfrac{1}{\sqrt{3}}|[\tfrac{1}{2}p_z + \tfrac{\sqrt{3}}{2}\tfrac{1}{\sqrt{2}}(s_1 - s_2)]\,\beta\rangle + \tfrac{1}{\sqrt{3}}|[\tfrac{1}{2}p_x + \tfrac{\sqrt{3}}{2}\tfrac{1}{\sqrt{2}}(s_1 + s_2)]\,\alpha\rangle + \tfrac{1}{\sqrt{3}}i|p_y\,\alpha\rangle,\\
|\phi_2 - i\rangle_L &= \tfrac{1}{\sqrt{3}}|[\tfrac{1}{2}p_z + \tfrac{\sqrt{3}}{2}\tfrac{1}{\sqrt{2}}(s_1 - s_2)]\,\alpha\rangle + \tfrac{1}{\sqrt{3}}|[\tfrac{1}{2}p_x + \tfrac{\sqrt{3}}{2}\tfrac{1}{\sqrt{2}}(s_1 + s_2)]\,\beta\rangle - \tfrac{1}{\sqrt{3}}i|p_y\,\beta\rangle.
\end{aligned}\right\}\quad(4.32)$$

Since these molecular orbitals are entirely delocalized, the bonding in the dihydride is more conveniently investigated by forming the more localized combinations

$$|L_1 \pm\rangle_L = \tfrac{1}{\sqrt{2}}(|\phi_1 i\rangle_L \pm |\phi_1 - i\rangle_L), \quad |L_2 \pm\rangle_L = \tfrac{1}{\sqrt{2}}(|\phi_2 i\rangle_L \pm |\phi_2 - i\rangle_L)$$

given by

$$\left.\begin{aligned}
|L_1 +\rangle_L &= \tfrac{1}{\sqrt{2}}|[\tfrac{1}{\sqrt{2}}\tfrac{1}{\sqrt{2}}(p_z + p_x) + \tfrac{1}{\sqrt{2}}s_1]\,\alpha\rangle - \tfrac{1}{\sqrt{2}}|[\tfrac{1}{\sqrt{2}}\tfrac{1}{\sqrt{2}}(p_x - p_z) + \tfrac{1}{\sqrt{2}}s_2]\,\beta\rangle,\\
|L_1 -\rangle_L &= \tfrac{1}{\sqrt{2}}|[\tfrac{1}{\sqrt{2}}\tfrac{1}{\sqrt{2}}(p_z + p_x) + \tfrac{1}{\sqrt{2}}s_1]\,\beta\rangle + \tfrac{1}{\sqrt{2}}|[\tfrac{1}{\sqrt{2}}\tfrac{1}{\sqrt{2}}(p_x - p_z) + \tfrac{1}{\sqrt{2}}s_2]\,\alpha\rangle,\\
|L_2 +\rangle_L &= \tfrac{1}{\sqrt{2}}|[\tfrac{1}{\sqrt{6}}\tfrac{1}{\sqrt{2}}(p_x + p_z) + \tfrac{1}{\sqrt{2}}s_1]\,\alpha\rangle + \tfrac{1}{\sqrt{2}}|[\tfrac{1}{\sqrt{6}}\tfrac{1}{\sqrt{2}}(p_x - p_z) + \tfrac{1}{\sqrt{2}}s_2]\,\beta\rangle\\
&\quad + \tfrac{1}{\sqrt{6}}i(|p_y\,\alpha\rangle - |p_y\,\beta\rangle),\\
|L_2 -\rangle_L &= -\tfrac{1}{\sqrt{2}}|[\tfrac{1}{\sqrt{6}}\tfrac{1}{\sqrt{2}}(p_x + p_z) + \tfrac{1}{\sqrt{2}}s_1]\,\beta\rangle + \tfrac{1}{\sqrt{2}}|[\tfrac{1}{\sqrt{6}}\tfrac{1}{\sqrt{2}}(p_x - p_z) + \tfrac{1}{\sqrt{2}}s_2]\,\alpha\rangle\\
&\quad + \tfrac{1}{\sqrt{6}}i(|p_y\,\alpha\rangle + |p_y\,\beta\rangle).
\end{aligned}\right\}\quad(4.33)$$

These results show, since the orbitals $\frac{1}{\sqrt{2}}(p_z + p_x)$ and $\frac{1}{\sqrt{2}}(p_x - p_z)$ are p orbitals orientated along the E–H_1 and E–H_2 bonds, that the two orbitals $|L_1 +\rangle_L$ and $|L_1 -\rangle_L$ are both equal mixtures of two fully bonding localized molecular orbitals while $|L_2 +\rangle_L$ and $|L_2 -\rangle_L$ have non-bonding p_y-components. Since the non-bonding fraction is $\frac{1}{3}$, this might suggest that the order of each E–H bond is $\frac{5}{6}$ because occupation of the fully bonding localized orbital $|L_1 +\rangle$ by one electron contributes $\frac{1}{2}$ to the order of each E–H bond. However, the bonding properties of the molecular orbitals $|L_2 \pm\rangle_L$ must be still further reduced compared with those of $|L_1 \pm\rangle$ because if the orbital $\frac{1}{\sqrt{2}}[\frac{1}{\sqrt{2}}(p_x + p_z) + s_1]$ is fully bonding then the normalized orbital $\frac{1}{\sqrt{2}}N[\frac{1}{\sqrt{6}}(p_z + p_x) + s_1]$ (N is a normalization constant) cannot also have this property. The latter orbital is a linear combination of the fully bonding orbital $\frac{1}{\sqrt{2}}[\frac{1}{\sqrt{2}}(p_x + p_z) + s_1]$ plus the corresponding fully anti-bonding orbital. Although it might not be useful to pursue this observation quantitatively, it should be pointed out that the prediction that the bond order is further reduced by anti-bonding terms exactly parallels that made by the Kappa valence method.

The identity between the molecular orbitals (4.31) and the forms for the molecular orbitals suggested by examining the Kappa-valence method is evidence that both the equilibrium bond angle predicted and the molecular orbitals calculated by neglecting overlap are not artifacts of this neglect. Since it is the overlap between the spin orbitals $|\frac{1}{\sqrt{2}}(p_x + p_z)\,\alpha\rangle$ and $|s_1\,\alpha\rangle$

that is responsible for the bonding of the first hydrogen atom in the non-relativistic wavefunction (4.24), it follows that the localized molecular orbitals corresponding to the bonds are $\frac{1}{\sqrt{2}}(|\frac{1}{\sqrt{2}}(p_x+p_z)\,\alpha\rangle+|s_1\alpha\rangle)$ and $\frac{1}{\sqrt{2}}(|\frac{1}{\sqrt{2}}(p_x-p_z)\,\alpha\rangle+|s_2\alpha\rangle)$. The delocalized molecular orbitals can then be calculated as linear combinations of the localized ones. The localized relativistic molecular orbitals derived from the wavefunction (4.12), after use of the results $c_3 = c_4 = \frac{1}{\sqrt{2}}$, therefore take the form

$$\left.\begin{aligned}|l_1+\rangle &= S'\tfrac{1}{\sqrt{2}}[|t_1\rangle+\tfrac{1}{\sqrt{2}}(|s_1\tfrac{1}{2}\rangle-|s_1-\tfrac{1}{2}\rangle)],\\ |l_1-\rangle &= S'\tfrac{1}{\sqrt{2}}[-|t_2\rangle+\tfrac{1}{\sqrt{2}}(|s_1\tfrac{1}{2}\rangle+|s_1-\tfrac{1}{2}\rangle)],\\ |l_2+\rangle &= S'\tfrac{1}{\sqrt{2}}[|t_3\rangle+\tfrac{1}{\sqrt{2}}(|s_2\tfrac{1}{2}\rangle+|s_2-\tfrac{1}{2}\rangle)],\\ |l_2-\rangle &= S'\tfrac{1}{\sqrt{2}}[-|t_4\rangle+\tfrac{1}{\sqrt{2}}(-|s_2\tfrac{1}{2}\rangle+|s_2-\tfrac{1}{2}\rangle)],\end{aligned}\right\}. \tag{4.34}$$

from which the delocalized orbitals

$$\left.\begin{aligned}|\phi_1 i\rangle &= \tfrac{1}{\sqrt{2}}K'(|l_1-\rangle-|l_2-\rangle), & |\phi_2 i\rangle &= \tfrac{1}{\sqrt{2}}K(|l_1+\rangle+|l_2+\rangle),\\ |\phi_1 -i\rangle &= \tfrac{1}{\sqrt{2}}K'(|l_1+\rangle-|l_2+\rangle), & |\phi_2 -i\rangle &= \tfrac{1}{\sqrt{2}}K(|l_1-\rangle+|l_2-\rangle)\end{aligned}\right\} \tag{4.35}$$

are derived. Here S', K and K' are normalization constants which become unity in the limit of small overlaps $\langle t_i|s_\mu m\rangle$. The results (4.34) show, after substitution of the forms (4.18) for the hybrids $|t_i\rangle$, that the molecular orbitals $|\phi_1 i\rangle$ and $|\phi_2 i\rangle$, (4.35), are identical to (4.31*a*) and (4.31*b*) respectively, after (4.31*a*) is multiplied by $K'S'$ and (4.31*b*) is multiplied by KS'. The factors $K'S'$ and KS' become unity if overlap is neglected so that the molecular orbital and Kappa valence methods yield the same result when the identical neglect of overlap approximation is made in both approaches.

5. CLOSED $\bar{p}^2$ SUBSHELLS

In this section the Kappa valence method is used to examine whether an element described in Dirac–Fock theory as having two valence $\bar{p}$ electrons, which therefore constitute a closed $\bar{p}^2$ subshell, can form a covalent bond to a hydrogen atom without invoking a valence state in which electrons are partially promoted from $\bar{p}$ into p orbitals. Non-relativistic molecular orbital theory, in its simplest form, predicts the bond order in the unknown HeH molecule to be one half whereas valence bond theory unambiguously predicts that the He–H potential energy curve is purely repulsive. This shows that the interaction between a closed $\bar{p}^2$ subshell and a hydrogen atom is much better investigated by using the Kappa valence method than by using relativistic molecular orbital theory.

The Kappa valence wavefunction describing the interaction of a hydrogen atom with the ground state of a heavy element having two $\bar{p}$ valence electrons is

$$|\psi_{\kappa v}\rangle = S\hat{\mathscr{A}}(|\mathrm{core}\rangle|\bar{p}\tfrac{1}{2}\rangle|\bar{p}-\tfrac{1}{2}\rangle|s-\tfrac{1}{2}\rangle). \tag{5.1}$$

Here S is the normalization constant given by

$$S = (1-\langle s-\tfrac{1}{2}|\bar{p}-\tfrac{1}{2}\rangle^2)^{-\frac{1}{2}}, \tag{5.2}$$

if the overlaps between the core orbitals and the hydrogen orbital are neglected. With this assumption, the purely electronic energy of $|\psi_{\kappa v}\rangle$ obtained as the expectation value over the

Brown hamiltonian is found (stage 1 of § 3 (*a*)) to be

$$\begin{aligned} E_{\kappa\mathrm{v}} = {} & \mathrm{S}^2[(1-\langle \mathrm{s}-\tfrac{1}{2}|\bar{\mathrm{p}}-\tfrac{1}{2}\rangle^2)(E_{\mathrm{core}}+\sum_{\mathrm{c}}\langle \mathrm{c}|\hat{V}_{\mathrm{H}}|\mathrm{c}\rangle+\langle \bar{\mathrm{p}}\tfrac{1}{2}|\hat{\mathscr{H}}_{\mathrm{D}}+\hat{V}_{\mathrm{DFCE}}|\bar{\mathrm{p}}\tfrac{1}{2}\rangle) \\ & +\langle \bar{\mathrm{p}}-\tfrac{1}{2}|\hat{\mathscr{H}}_{\mathrm{D}}+\hat{V}_{\mathrm{DFCE}}|\bar{\mathrm{p}}-\tfrac{1}{2}\rangle+\langle \mathrm{s}-\tfrac{1}{2}|\hat{\mathscr{H}}_{\mathrm{D}}+\hat{V}_{\mathrm{DFCE}}|\mathrm{s}-\tfrac{1}{2}\rangle+\langle \bar{\mathrm{p}}\tfrac{1}{2}\bar{\mathrm{p}}-\tfrac{1}{2}|r_{12}^{-1}|\bar{\mathrm{p}}\tfrac{1}{2}\bar{\mathrm{p}}-\tfrac{1}{2}\rangle \\ & -\langle \bar{\mathrm{p}}\tfrac{1}{2}\bar{\mathrm{p}}-\tfrac{1}{2}|r_{12}^{-1}|\bar{\mathrm{p}}-\tfrac{1}{2}\bar{\mathrm{p}}\tfrac{1}{2}\rangle+\langle \bar{\mathrm{p}}\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}|r_{12}^{-1}|\bar{\mathrm{p}}\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}\rangle-\langle \bar{\mathrm{p}}\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{s}-\tfrac{1}{2}\bar{\mathrm{p}}\tfrac{1}{2}\rangle \\ & +\langle \bar{\mathrm{p}}-\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}|r_{12}^{-1}|\bar{\mathrm{p}}-\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}\rangle-\langle \bar{\mathrm{p}}-\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{s}-\tfrac{1}{2}\bar{\mathrm{p}}-\tfrac{1}{2}\rangle-2\langle \bar{\mathrm{p}}-\tfrac{1}{2}|\mathrm{s}-\tfrac{1}{2}\rangle \\ & \times(\langle \mathrm{s}-\tfrac{1}{2}|\hat{\mathscr{H}}_{\mathrm{D}}+\hat{V}_{\mathrm{DFCE}}|\bar{\mathrm{p}}-\tfrac{1}{2}\rangle+\langle \bar{\mathrm{p}}\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}|r_{12}^{-1}|\bar{\mathrm{p}}\tfrac{1}{2}\bar{\mathrm{p}}-\tfrac{1}{2}\rangle-\langle \bar{\mathrm{p}}\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}|r_{12}^{-1}|\bar{\mathrm{p}}-\tfrac{1}{2}\bar{\mathrm{p}}\tfrac{1}{2}\rangle)], \end{aligned} \tag{5.3}$$

where all the orbitals used to construct the wavefunction (5.1) are taken to lie entirely within some positive-energy subspace. In (5.3) $\hat{\mathscr{H}}_{\mathrm{D}}$ is the one-electron hamiltonian (2.3) and $\hat{V}_{\mathrm{DFCE}}$ ($=\Sigma_{\mathrm{c}}\hat{\mathrm{J}}_{\mathrm{c}}-\hat{\mathrm{K}}_{\mathrm{c}}$) is the electronic Dirac–Fock potential generated by the core orbitals. The $\bar{\mathrm{p}}$ valence orbitals of the heavy element (E) satisfy the atomic Dirac–Fock equations

$$(\hat{\mathscr{H}}_{\mathrm{k.e.}}+\hat{V}_{\mathrm{NE}}+\hat{V}_{\mathrm{DFE}})\,|\bar{\mathrm{p}}m\rangle = \epsilon_{\bar{\mathrm{p}}}|\bar{\mathrm{p}}m\rangle, \tag{5.4a}$$

with

$$\hat{V}_{\mathrm{DFE}} = \hat{V}_{\mathrm{DFCE}}+\sum_{m=\pm\frac{1}{2}}(\hat{\mathrm{J}}_{\bar{\mathrm{p}}m}-\hat{\mathrm{K}}_{\bar{\mathrm{p}}m}) \tag{5.4b}$$

which contain no off-diagonal Lagrange multipliers because the core $\bar{\mathrm{p}}^2$ configuration of the heavy element contains only closed subshells. As a preliminary to extracting the interaction energy it is useful to rewrite (5.3) in terms of the potential energy operator $\hat{V}_{\mathrm{DFE}}$

$$\begin{aligned} E_{\kappa\mathrm{v}} = {} & E_{\mathrm{core}}+\sum_{\mathrm{c}}\langle \mathrm{c}|\hat{V}_{\mathrm{H}}|\mathrm{c}\rangle+\langle \bar{\mathrm{p}}\tfrac{1}{2}|\hat{\mathscr{H}}_{\mathrm{D}}+\hat{V}_{\mathrm{DFE}}|\bar{\mathrm{p}}\tfrac{1}{2}\rangle-\langle \bar{\mathrm{p}}\tfrac{1}{2}\bar{\mathrm{p}}-\tfrac{1}{2}|r_{12}^{-1}|\bar{\mathrm{p}}\tfrac{1}{2}\bar{\mathrm{p}}-\tfrac{1}{2}\rangle \\ & +\langle \bar{\mathrm{p}}\tfrac{1}{2}\bar{\mathrm{p}}-\tfrac{1}{2}|r_{12}^{-1}|\bar{\mathrm{p}}-\tfrac{1}{2}\bar{\mathrm{p}}\tfrac{1}{2}\rangle+S^2[\langle \bar{\mathrm{p}}-\tfrac{1}{2}|\hat{\mathscr{H}}_{\mathrm{D}}+\hat{V}_{\mathrm{DFE}}|\bar{\mathrm{p}}-\tfrac{1}{2}\rangle \\ & +\langle \mathrm{s}-\tfrac{1}{2}|\hat{\mathscr{H}}_{\mathrm{D}}+\hat{V}_{\mathrm{DFE}}|\mathrm{s}-\tfrac{1}{2}\rangle-2\langle \bar{\mathrm{p}}-\tfrac{1}{2}|\mathrm{s}-\tfrac{1}{2}\rangle\langle \mathrm{s}-\tfrac{1}{2}|\hat{\mathscr{H}}_{\mathrm{D}}+\hat{V}_{\mathrm{DFE}}|\bar{\mathrm{p}}-\tfrac{1}{2}\rangle], \end{aligned} \tag{5.5}$$

where (5.2) has been used. The interaction energy is extracted (stage 2) from the total energy ($E_{\mathrm{T}\kappa\mathrm{v}}$), obtained by addition of the internuclear repulsion, Z_{E}/R to the electronic energy $E_{\kappa\mathrm{v}}$, by making the usual assumption that the core orbitals do not overlap with the hydrogen orbital so that

$$\sum_{\mathrm{c}}\langle \mathrm{c}|\hat{V}_{\mathrm{H}}|\mathrm{c}\rangle = -(Z_{\mathrm{E}}-2)/R. \tag{5.6}$$

This result taken in conjunction with (3.7*b*) and (5.4*a*) enables (5.5) to be expressed as

$$\begin{aligned} E_{\mathrm{T}\kappa\mathrm{v}} = {} & E_{\mathrm{core}}+2\epsilon_{\bar{\mathrm{p}}}-\langle \bar{\mathrm{p}}\tfrac{1}{2}\bar{\mathrm{p}}-\tfrac{1}{2}|r_{12}^{-1}|\bar{\mathrm{p}}\tfrac{1}{2}\bar{\mathrm{p}}-\tfrac{1}{2}\rangle+\langle \bar{\mathrm{p}}\tfrac{1}{2}\bar{\mathrm{p}}-\tfrac{1}{2}|r_{12}^{-1}|\bar{\mathrm{p}}-\tfrac{1}{2}\bar{\mathrm{p}}\tfrac{1}{2}\rangle+E_{\mathrm{H}} \\ & +\langle \bar{\mathrm{p}}\tfrac{1}{2}|\hat{V}_{\mathrm{H}}|\bar{\mathrm{p}}\tfrac{1}{2}\rangle+R^{-1}+S^2[\langle \bar{\mathrm{p}}-\tfrac{1}{2}|\hat{V}_{\mathrm{H}}|\bar{\mathrm{p}}-\tfrac{1}{2}\rangle+\langle \mathrm{s}-\tfrac{1}{2}|\hat{V}_{\mathrm{NE}}+\hat{V}_{\mathrm{DFE}}|\mathrm{s}-\tfrac{1}{2}\rangle \\ & -\langle \bar{\mathrm{p}}-\tfrac{1}{2}|\mathrm{s}-\tfrac{1}{2}\rangle\langle \mathrm{s}-\tfrac{1}{2}|\hat{V}_{\mathrm{H}}+\hat{V}_{\mathrm{NE}}+\hat{V}_{\mathrm{DFE}}|\bar{\mathrm{p}}-\tfrac{1}{2}\rangle]+R^{-1}. \end{aligned} \tag{5.7}$$

By noting that the total energy E_{E} of the isolated heavy element can be expressed as

$$E_{\mathrm{E}} = E_{\mathrm{core}}+2\epsilon_{\bar{\mathrm{p}}}-\langle \bar{\mathrm{p}}\tfrac{1}{2}\bar{\mathrm{p}}-\tfrac{1}{2}|r_{12}^{-1}|\bar{\mathrm{p}}\tfrac{1}{2}\bar{\mathrm{p}}-\tfrac{1}{2}\rangle+\langle \bar{\mathrm{p}}\tfrac{1}{2}\bar{\mathrm{p}}-\tfrac{1}{2}|r_{12}^{-1}|\bar{\mathrm{p}}-\tfrac{1}{2}\bar{\mathrm{p}}\tfrac{1}{2}\rangle, \tag{5.8}$$

the result (5.7) shows, when taken in conjunction with (5.4*b*), that the interaction energy is given by

$$\begin{aligned} E_{\mathrm{int}} = {} & \langle \bar{\mathrm{p}}\tfrac{1}{2}|\hat{V}_{\mathrm{H}}|\bar{\mathrm{p}}\tfrac{1}{2}\rangle+R^{-1}+S^2[\langle \bar{\mathrm{p}}-\tfrac{1}{2}|\hat{V}_{\mathrm{H}}|\bar{\mathrm{p}}-\tfrac{1}{2}\rangle+\langle \mathrm{s}-\tfrac{1}{2}|\hat{V}_{\mathrm{NE}}+\hat{V}_{\mathrm{DFCE}}|\mathrm{s}-\tfrac{1}{2}\rangle \\ & +\langle \mathrm{s}-\tfrac{1}{2}\bar{\mathrm{p}}\tfrac{1}{2}|r_{12}^{-1}|\mathrm{s}-\tfrac{1}{2}\bar{\mathrm{p}}\tfrac{1}{2}\rangle-\langle \mathrm{s}-\tfrac{1}{2}\bar{\mathrm{p}}\tfrac{1}{2}|r_{12}^{-1}|\bar{\mathrm{p}}\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}\rangle+\langle \mathrm{s}-\tfrac{1}{2}\bar{\mathrm{p}}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{s}-\tfrac{1}{2}\bar{\mathrm{p}}-\tfrac{1}{2}\rangle \\ & -\langle \mathrm{s}-\tfrac{1}{2}\bar{\mathrm{p}}-\tfrac{1}{2}|r_{12}^{-1}|\bar{\mathrm{p}}-\tfrac{1}{2}\mathrm{s}-\tfrac{1}{2}\rangle-\langle \bar{\mathrm{p}}-\tfrac{1}{2}|\mathrm{s}-\tfrac{1}{2}\rangle(\langle \mathrm{s}-\tfrac{1}{2}|\hat{V}_{\mathrm{H}}+\hat{V}_{\mathrm{NE}}+\hat{V}_{\mathrm{DFCE}}|\bar{\mathrm{p}}-\tfrac{1}{2}\rangle \\ & +\langle \mathrm{s}-\tfrac{1}{2}\bar{\mathrm{p}}\tfrac{1}{2}|r_{12}^{-1}|\bar{\mathrm{p}}-\tfrac{1}{2}\bar{\mathrm{p}}\tfrac{1}{2}\rangle-\langle \mathrm{s}-\tfrac{1}{2}\bar{\mathrm{p}}\tfrac{1}{2}|r_{12}^{-1}|\bar{\mathrm{p}}\tfrac{1}{2}\bar{\mathrm{p}}-\tfrac{1}{2}\rangle)]+R^{-1}. \end{aligned} \tag{5.9}$$

After retaining only the large components and using the results (3.9) (stage 3), this interaction energy is transparently written in terms of purely spatial integrals as

$$E_{\mathrm{int}} = \tfrac{1}{3}(\langle \mathrm{p}_0|\hat{V}_{\mathrm{H}}|\mathrm{p}_0\rangle + R^{-1}) + \tfrac{2}{3}(\langle \mathrm{p}_1|\hat{V}_{\mathrm{H}}|\mathrm{p}_1\rangle + R^{-1}) + \tfrac{1}{3}[N_{\mathrm{T}}(\mathrm{s}_0, \mathrm{p}_0, \tfrac{1}{3}) + N'_{\mathrm{T}}] + \tfrac{2}{3}(O_{\mathrm{T}} + C_{\mathrm{T}}), \tag{5.10}$$

where

$$\begin{aligned} N_{\mathrm{T}}(\mathrm{a}_1 \mathrm{b}_1 \mathrm{k}) = {} & (1 - \mathrm{k}\langle \mathrm{a}|\mathrm{b}\rangle^2)^{-1}(\langle \mathrm{b}|\hat{V}_{\mathrm{H}}|\mathrm{b}\rangle + \langle \mathrm{a}|\tfrac{1}{2}\hat{V}_{\mathrm{E}}|\mathrm{a}\rangle + \langle \mathrm{ab}|r_{12}^{-1}|\mathrm{ab}\rangle + R^{-1} \\ & - \langle \mathrm{a}|\mathrm{b}\rangle\langle \mathrm{b}|\hat{V}_{\mathrm{H}} + \tfrac{1}{2}\hat{V}_{\mathrm{E}} + R^{-1}|\mathrm{a}\rangle - \langle \mathrm{ab}|r_{12}^{-1}|\mathrm{ba}\rangle), \end{aligned} \tag{5.11a}$$

$$\begin{aligned} N'_{\mathrm{T}} = {} & (1 - \tfrac{1}{3}\langle \mathrm{s}_0|\mathrm{p}_0\rangle^2)^{-1}[\langle \mathrm{s}_0|\tfrac{1}{2}\hat{V}_{\mathrm{E}}|\mathrm{s}_0\rangle + \langle \mathrm{s}_0\mathrm{p}_0|r_{12}^{-1}|\mathrm{s}_0\mathrm{p}_0\rangle \\ & - \langle \mathrm{p}_0|\mathrm{s}_0\rangle(\langle \mathrm{s}_0|\tfrac{1}{2}\hat{V}_{\mathrm{E}}|\mathrm{p}_0\rangle + \tfrac{1}{3}\langle \mathrm{s}_0\mathrm{p}_0|r_{12}^{-1}|\mathrm{p}_0\mathrm{p}_0\rangle + \tfrac{2}{3}\langle \mathrm{s}_0\mathrm{p}_1|r_{12}^{-1}|\mathrm{p}_0\mathrm{p}_1\rangle)], \end{aligned} \tag{5.11b}$$

$$\begin{aligned} O_{\mathrm{T}} = {} & (1 - \tfrac{1}{3}\langle \mathrm{s}_0|\mathrm{p}_0\rangle^2)^{-1}(\langle \mathrm{p}_1|\hat{V}_{\mathrm{H}}|\mathrm{p}_1\rangle + \langle \mathrm{s}_0|\tfrac{1}{2}\hat{V}_{\mathrm{E}}|\mathrm{s}_0\rangle + \langle \mathrm{s}_0\mathrm{p}_1|r_{12}^{-1}|\mathrm{s}_0\mathrm{p}_1\rangle \\ & + R^{-1} - \langle \mathrm{s}_0\mathrm{p}_1|r_{12}^{-1}|\mathrm{p}_1\mathrm{s}_0\rangle), \end{aligned} \tag{5.11c}$$

$$C_{\mathrm{T}} = (1 - \tfrac{1}{3}\langle \mathrm{s}_0|\mathrm{p}_0\rangle^2)^{-1}(\langle \mathrm{s}_0|\tfrac{1}{2}\hat{V}_{\mathrm{E}}|\mathrm{s}_0\rangle + \langle \mathrm{s}_0\mathrm{p}_1|r_{12}^{-1}|\mathrm{s}_0\mathrm{p}_1\rangle). \tag{5.11d}$$

Here $\hat{V}_{\mathrm{E}}$ consists of the direct potential arising from the nucleus and the core of the heavy element plus the exchange potential generated by the core large components in accordance with (3.10*c*) and (3.10*d*). The utility of the decomposition (5.11) is that N_{T} and O_{T} are to within the overall factor $(1 - \tfrac{1}{3}\langle \mathrm{s}_0|\mathrm{p}_0\rangle^2)^{-1}$, which is close to unity, identical to the interaction energies (3.12) predicted by the non-orthogonal Heitler–London triplet and orthogonal triplet wavefunctions because the potential $\tfrac{1}{2}\hat{V}_{\mathrm{E}}$ behaves as $-1/r$ for large distances r from the nucleus of E. Hence, with the orders of pure non-orthogonal Heitler–London singlet and orthogonal triplet bonds taken to be -1 and $+\tfrac{1}{2}$ respectively, the order of the bond described by (5.1) is predicted to be zero if only the terms N_{T} and O_{T} are considered. Of the four remaining terms, both the first two terms in (5.10) and C_{T}, (5.11*d*), are just parts of a coulomb interaction while N'_{T} is composed of terms of the same form as those entering N_{T}. The latter is therefore almost certainly more important than the purely coulombic terms and consequently the bond order will be negative but greater than $-\tfrac{1}{3}$. Hence it has been shown that a closed $\bar{\mathrm{p}}^2$ subshell cannot form a covalent bond to a hydrogen atom when the electronic structure is adequately described by (5.1).

It is interesting to compare the wavefunction (5.1), for which the bond order is predicted to lie between $-\tfrac{1}{3}$ and zero, with the function

$$|\psi_{\kappa v}\mathrm{s}^2\rangle = S\mathscr{A}(|\mathrm{core}\rangle|\mathrm{s}_{\mathrm{E}}\tfrac{1}{2}\rangle|\mathrm{s}_{\mathrm{E}} -\tfrac{1}{2}\rangle|\mathrm{s} -\tfrac{1}{2}\rangle), \tag{5.12}$$

which describes the interaction between a hydrogen atom and an element having two s valence electrons. Although this function is built from Dirac–Fock orbitals, it does not differ from the function describing the repulsive interaction between a hydrogen atom and a helium atom. The interaction energy predicted by (5.12) is calculated by the methods used to derive (5.10) to be

$$E_{\mathrm{int}}(\mathrm{s}^2) = \langle \mathrm{s}_{\mathrm{E}0}|\hat{V}_{\mathrm{H}}|\mathrm{s}_{\mathrm{E}0}\rangle + R^{-1} + N_{\mathrm{T}}(\mathrm{s}_0, \mathrm{s}_{0\mathrm{E}}, 1) + N'_{\mathrm{T}1}, \tag{5.13}$$

$$\begin{aligned} N'_{\mathrm{T}1} = {} & (1 - \langle \mathrm{s}_0|\mathrm{s}_{0\mathrm{E}}\rangle^2)^{-1}[\langle \mathrm{s}_{0\mathrm{E}}|\tfrac{1}{2}\hat{V}_{\mathrm{E}}|\mathrm{s}_0\rangle + \langle \mathrm{s}_0\mathrm{s}_{0\mathrm{E}}|r_{12}^{-1}|\mathrm{s}_0\mathrm{s}_{0\mathrm{E}}\rangle \\ & - \langle \mathrm{s}_{0\mathrm{E}}|\mathrm{s}_0\rangle(\langle \mathrm{s}_0|\tfrac{1}{2}\hat{V}_{\mathrm{E}}|\mathrm{s}_{0\mathrm{E}}\rangle + \langle \mathrm{s}_0\mathrm{s}_{0\mathrm{E}}|r_{12}^{-1}|\mathrm{s}_{0\mathrm{E}}\mathrm{s}_{0\mathrm{E}}\rangle)], \end{aligned} \tag{5.14}$$

where $\mathrm{s}_{0\mathrm{E}}$ is the purely spatial function used to construct the large components of the orbitals $|\mathrm{s}_{\mathrm{E}} \pm \tfrac{1}{2}\rangle$. Since the energy $E_{\mathrm{int}}(\mathrm{s}^2)$ consists of a non-orthogonal Heitler–London triplet repulsive term plus a similar contribution $N'_{\mathrm{T}1}$, the potential energy curve for the interaction of a hydrogen atom with the ground state of an element having an s^2 valence configuration is predicted to be strongly repulsive, the bond order being at least -1. The wavefunction (5.12) differs from (5.1) because spin orthogonality ensures that the exchange interaction between the large components of $|\mathrm{s}-\tfrac{1}{2}\rangle$ and $|\mathrm{s}_{\mathrm{E}}\tfrac{1}{2}\rangle$ vanishes whereas the corresponding exchange interaction between $|\mathrm{s}-\tfrac{1}{2}\rangle$ and $|\bar{\mathrm{p}}\tfrac{1}{2}\rangle$ in (5.9) is non-zero. Indeed it is the $|\mathrm{p}_1\,\beta\rangle$ portion of the large components of $|\bar{\mathrm{p}}\tfrac{1}{2}\rangle$ that gives rise to the orthogonal triplet contribution to the interaction energy (5.10). The differences between the interaction energies (5.10) and (5.13), and hence in the bond orders, show that an element having a closed s^2 valence subshell will repel a hydrogen atom more strongly than a heavy element having a closed $\bar{\mathrm{p}}^2$ valence subshell. This difference suggests that although there is clearly an analogy between a valence inert gas configuration and the valence $\bar{\mathrm{p}}^2$ configuration this analogy is not altogether complete.

6. BONDING IN MONOHALIDES

(a) *The Kappa valence description of monohalides*

(i) *Interaction with the normal halogen valence state*

In this section the Kappa valence method is used to investigate the purely covalent bonding between a halogen and the *j–j* coupled ground state of an element having a single valence electron occupying a Dirac–Fock $\bar{\mathrm{p}}$ or p orbital. It will be assumed that the energy separation between the $\bar{\mathrm{p}}$ orbitals, denoted $|\bar{\mathrm{p}}_{\mathrm{H}}m\rangle$, and the p orbitals, denoted $|\mathrm{p}_{\mathrm{H}}m\rangle$, of the halogen is negligible. This investigation also reveals the nature of the bonding between such a heavy element and a group containing both a single electron in a σ orbital and a filled shell of 4π electrons for which the π–σ energy separation is large.

The halogen Dirac–Fock atomic orbitals are taken to have the standard central field form (2.24) as implied by the notation $|\bar{\mathrm{p}}_{\mathrm{H}}m\rangle$ and $|\mathrm{p}_{\mathrm{H}}m\rangle$. Consequently these orbitals are eigenfunctions of a Fock operator that commutes with $\hat{\mathrm{j}}^2$ as well as $\hat{\mathrm{j}}_z$. Such a Fock operator arises naturally by demanding that the average (E_{av}) of the energies of the six single determinants of Dirac spinors, which can be constructed by placing five electrons in the six available valence orbitals, be stationary with respect to small variations of the orbitals. The state in which the valence orbital $|\mathrm{w}\rangle$, where $|\mathrm{w}\rangle$ can be either of the two orbitals $|\bar{\mathrm{p}}_{\mathrm{H}}m\rangle$ or any of the four orbitals $|\mathrm{p}_{\mathrm{H}}m\rangle$, is unoccupied is denoted $|\mathrm{w}_{\mathrm{vac}}\rangle$. Then defining the generalized electron repulsion operator $\hat{\mathrm{G}}_{\mathrm{w,\,w}}$, and the rotational invariant potential $\hat{V}^{(0)}_{\mathrm{VH}}$ through

$$\hat{\mathrm{G}}_{\mathrm{w,\,w'}}(r_1) = \int \mathrm{w}(r_2)^{+}[r_{12}^{-1}(1-\hat{\mathrm{P}}_{12})]\,\mathrm{w}'(r_2)\,\mathrm{d}r_2, \tag{6.1}$$

$$\hat{V}^{(0)}_{\mathrm{VH}} = \sum_{\mathrm{w}=1}^{6} \hat{\mathrm{G}}_{\mathrm{w,\,w}}, \tag{6.2}$$

where $\hat{\mathrm{P}}_{12}$ is the operator interchanging labels 1 and 2, it follows that the average energy (E_{av}) can be expressed as

$$\begin{aligned} E_{\mathrm{av}} &= \frac{1}{6}\sum_{\mathrm{w}=1}^{6} E(\mathrm{w}_{\mathrm{vac}}) = \frac{1}{6}\sum_{\mathrm{w}=1}^{6}\sum_{\mathrm{w}'\neq\mathrm{w}} \langle \mathrm{w}'|\hat{\mathscr{H}}_{\mathrm{k.e.}}+\hat{V}_{\mathrm{NH}}+\hat{V}_{\mathrm{CHDF}}+\hat{V}^{(0)}_{\mathrm{VH}}-\hat{\mathrm{G}}_{\mathrm{w,\,w}}|\mathrm{w}'\rangle \\ &= \frac{1}{6}\sum_{\mathrm{w}=1}^{6}\sum_{\mathrm{w}'\neq\mathrm{w}} \langle \mathrm{w}'|\hat{\mathscr{H}}_{\mathrm{k.e.}}+\hat{V}_{\mathrm{NH}}+\hat{V}_{\mathrm{CHDF}}|\mathrm{w}'\rangle + \frac{2}{3}\sum_{\mathrm{w}=1}^{6}\langle \mathrm{w}|\hat{\mathrm{J}}^{(0)}_{\mathrm{VH}}|\mathrm{w}\rangle, \end{aligned} \tag{6.3}$$

where $\hat{V}_{\mathrm{NH}}$ and $\hat{V}_{\mathrm{CHDF}}$ are respectively the nuclear potential and the Dirac–Fock potential due to the halogen core orbitals. After introducing the Lagrange multipliers $\epsilon_{\mathrm{c_H w}}$ to retain core–valence orthogonality, standard techniques show that the orbitals that render the average energy (6.3) stationary satisfy

$$(\mathscr{H}_{\mathrm{k.e.}}+\hat{V}_{\mathrm{NH}}+\hat{V}_{\mathrm{CHDF}}+\tfrac{4}{5}\hat{V}^{(0)}_{\mathrm{VH}})\,|\mathrm{w}m_{\mathrm{w}}\rangle = \epsilon_{\mathrm{w}}|\mathrm{w}m_{\mathrm{w}}\rangle+\sum_{\mathrm{c_H}}\epsilon_{\mathrm{c_H w}}|\mathrm{c_H}\rangle, \tag{6.4}$$

where $|\mathrm{c_H}\rangle$ denotes a halogen core orbital. The Dirac–Fock configuration corresponding to the $\pi^4\mathrm{p}_z$ non-relativistic valence state of a halogen is constructed by introducing the four-component orbitals $|\xi m_{\mathrm{H}}\rangle$ of m_j quantum number m_{H} where ξ is a label denoting the spatial symmetry of the large components. Thus one can usefully define

$$\left.\begin{aligned}
|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle &= \sqrt{\tfrac{2}{3}}|\bar{\mathrm{p}}_{\mathrm{H}}\tfrac{1}{2}\rangle+\tfrac{1}{\sqrt{3}}|\mathrm{p}_{\mathrm{H}}\tfrac{1}{2}\rangle,\\
|\pi_{-1,\mathrm{H}}-\tfrac{1}{2}\rangle &= -\sqrt{\tfrac{2}{3}}|\bar{\mathrm{p}}_{\mathrm{H}}-\tfrac{1}{2}\rangle+\tfrac{1}{\sqrt{3}}|\mathrm{p}_{\mathrm{H}}-\tfrac{1}{2}\rangle,\\
|z_{\mathrm{H}}\tfrac{1}{2}\rangle &= -\tfrac{1}{\sqrt{3}}|\bar{\mathrm{p}}_{\mathrm{H}}\tfrac{1}{2}\rangle+\sqrt{\tfrac{2}{3}}|\mathrm{p}_{\mathrm{H}}\tfrac{1}{2}\rangle,\\
|z_{\mathrm{H}}-\tfrac{1}{2}\rangle &= \tfrac{1}{\sqrt{3}}|\bar{\mathrm{p}}_{\mathrm{H}}-\tfrac{1}{2}\rangle+\sqrt{\tfrac{2}{3}}|\mathrm{p}_{\mathrm{H}}-\tfrac{1}{2}\rangle
\end{aligned}\right\} \tag{6.5}$$

because the large components (3.9) show that

$$\left.\begin{aligned}
|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle_{\mathrm{L}} &= |\mathrm{p}_{1,\mathrm{H}}\beta\rangle, & |z_{\mathrm{H}}\tfrac{1}{2}\rangle_{\mathrm{L}} &= |\mathrm{p}_{0,\mathrm{H}}\alpha\rangle,\\
|\pi_{-1,\mathrm{H}}-\tfrac{1}{2}\rangle_{\mathrm{L}} &= |\mathrm{p}_{-1,\mathrm{H}}\alpha\rangle, & |z_{\mathrm{H}}-\tfrac{1}{2}\rangle_{\mathrm{L}} &= |\mathrm{p}_{0,\mathrm{H}}\beta\rangle,
\end{aligned}\right\} \tag{6.6}$$

where $\mathrm{p}_{\pm 1,\mathrm{H}}$ and $\mathrm{p}_{0,\mathrm{H}}$ are purely spatial halogen valence orbitals having m_1 quantum numbers of ± 1 and zero respectively. The large components (6.6) of the orbitals (6.5) show that the Kappa valence wavefunction

$$\begin{aligned}
|\psi_{\kappa\mathrm{v}z}\rangle = S\hat{\mathscr{A}}[&|\mathrm{core}\rangle|\mathrm{core_H}\rangle|\mathrm{p_H}\tfrac{3}{2}\rangle|\mathrm{p_H}-\tfrac{3}{2}\rangle|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle|\pi_{-1,\mathrm{H}}-\tfrac{1}{2}\rangle\\
&\times\tfrac{1}{\sqrt{2}}(|\mathrm{v}\tfrac{1}{2}\rangle|z_{\mathrm{H}}-\tfrac{1}{2}\rangle\pm|\mathrm{v}-\tfrac{1}{2}\rangle|z_{\mathrm{H}}\tfrac{1}{2}\rangle)] \equiv \tfrac{1}{\sqrt{2}}S(|\Phi_1\rangle+(\Phi_2\rangle)
\end{aligned} \tag{6.7}$$

describes the formation of a covalent bond between the *j–j* coupled ground state of a heavy element having a single valence $\bar{\mathrm{p}}$ or p electron and a halogen in its normal valence state ($\pi^4\mathrm{p}_z$) in which all the π orbitals are filled, leaving a single unpaired electron in a p_z orbital. Here S is a normalization constant (the positive sign is taken if $|\mathrm{v}\rangle$ is a $\bar{\mathrm{p}}$ orbital and the negative sign if it is a p orbital) while $|\mathrm{core_H}\rangle$ is the Hartree product built from the Dirac–Fock core orbitals of the halogen:

$$|\mathrm{core_H}\rangle = \prod_{i\in\mathrm{core_H}}(|\mathrm{c}_{\mathrm{H}i}(\boldsymbol{r}_i)\rangle). \tag{6.8}$$

The total electronic energy, predicted from (6.7) by taking its expectation value over the Brown hamiltonian, is the sum of the two terms $\langle\Phi_1|\mathscr{H}_{\mathrm{Br}}|\Phi_1\rangle$ $(=\langle\Phi_2|\mathscr{H}_{\mathrm{Br}}|\Phi_2\rangle)$ and $\langle\Phi_1|\mathscr{H}_{\mathrm{Br}}|\Phi_2\rangle$. All the orbitals entering $|\Phi_1\rangle$ are orthogonal except for the pair $|\mathrm{v}\tfrac{1}{2}\rangle$ and $|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle$ if the overlaps $\langle\mathrm{c}|\mathrm{c_H}\rangle$, $\langle\mathrm{c}|\xi m_{\mathrm{H}}\rangle$ and $\langle\mathrm{c_H}|\mathrm{v}\tfrac{1}{2}\rangle$, which involve core orbitals, are neglected. Standard techniques then show, with all the orbitals except $|\mathrm{v}\rangle$ and $|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle$ denoted by r, that

$$\langle\Phi_1|\Phi_1\rangle = 1-\langle\mathrm{v}\tfrac{1}{2}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle^2, \tag{6.9a}$$

$$\begin{aligned}
\langle\Phi_1|\mathscr{H}_{\mathrm{Br}}|\Phi_1\rangle = {} & (1-\langle\mathrm{v}\tfrac{1}{2}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle^2)\,E_{\mathrm{r}}+\langle\mathrm{v}\tfrac{1}{2}|\mathscr{H}_{\mathrm{D}}+\sum_{\mathrm{r}}\hat{\mathrm{G}}_{\mathrm{r,r}}|\mathrm{v}\tfrac{1}{2}\rangle\\
&+\langle\pi_{1,\mathrm{H}}\tfrac{1}{2}|\mathscr{H}_{\mathrm{D}}+\sum_{\mathrm{r}}\hat{\mathrm{G}}_{\mathrm{r,r}}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle-2\langle\mathrm{v}\tfrac{1}{2}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle\langle\pi_{1,\mathrm{H}}\tfrac{1}{2}|\mathscr{H}_{\mathrm{D}}+\sum_{\mathrm{r}}\hat{\mathrm{G}}_{\mathrm{r,r}}|\mathrm{v}\tfrac{1}{2}\rangle\\
&+\langle\pi_{1,\mathrm{H}}\tfrac{1}{2}\mathrm{v}\tfrac{1}{2}|r_{12}^{-1}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\mathrm{v}\tfrac{1}{2}\rangle-\langle\pi_{1,\mathrm{H}}\tfrac{1}{2}\mathrm{v}\tfrac{1}{2}|r_{12}^{-1}|\mathrm{v}\tfrac{1}{2}\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle,
\end{aligned} \tag{6.9b}$$

where E_{r} consists of all the terms involving solely the orbitals r. The terms involving the overlap $\langle \pi_{1,\mathrm{H}}\tfrac{1}{2}|\mathrm{v}\tfrac{1}{2}\rangle$ entering both the normalization integral and $\langle \Phi_1|\hat{\mathscr{H}}_{\mathrm{Br}}|\Phi_1\rangle$ are exactly analogous to those arising from the overlap of the hydrogen orbital $|\mathrm{s}-\tfrac{1}{2}\rangle$ with valence orbital $|\mathrm{s}_{\mathrm{E}}-\tfrac{1}{2}\rangle$ when the repulsive interaction energy of the wavefunction (5.12) describing the interaction of a hydrogen atom with a closed s^2 shell is calculated. It is therefore not surprising that the overlap $\langle \pi_{1,\mathrm{H}}\tfrac{1}{2}|\mathrm{v}\tfrac{1}{2}\rangle$ is responsible for a repulsive contribution to the interaction energy of the non-orthogonal Heitler–London triplet type. Evaluation of the overlap $\langle \Phi_1|\Phi_2\rangle$ and matrix element $\langle \Phi_1|\hat{\mathscr{H}}_{\mathrm{Br}}|\Phi_2\rangle$ is more tedious because the orbitals $|\mathrm{v}\pm\tfrac{1}{2}\rangle$ overlap both $|z_{\mathrm{H}}\pm\tfrac{1}{2}\rangle$ and $|\pi_{\pm1,\mathrm{H}}\pm\tfrac{1}{2}\rangle$. With the remaining orbitals denoted by p, each of which is taken to be orthogonal to all the remaining orbitals in (6.7), and with $\hat{\mathrm{h}}$ defined as

$$\hat{\mathrm{h}} = \hat{\mathscr{H}}_{\mathrm{D}} + \sum_{\mathrm{p}} \hat{\mathrm{G}}_{\mathrm{p,p}} \tag{6.10}$$

standard techniques show that

$$\langle \Phi_1|\Phi_2\rangle = -\langle z_{\mathrm{H}}-\tfrac{1}{2}|\mathrm{v}-\tfrac{1}{2}\rangle\langle \mathrm{v}\tfrac{1}{2}|z_{\mathrm{H}}\tfrac{1}{2}\rangle, \tag{6.11a}$$

$$\begin{aligned}\langle \Phi_1|\hat{\mathscr{H}}_{\mathrm{Br}}|\Phi_2\rangle = {} & -\langle z_{\mathrm{H}}-\tfrac{1}{2}|\mathrm{v}-\tfrac{1}{2}\rangle\langle \mathrm{v}\tfrac{1}{2}|z_{\mathrm{H}}\tfrac{1}{2}\rangle(\langle \pi_{1,\mathrm{H}}\tfrac{1}{2}|\hat{\mathrm{h}}+\hat{\mathrm{G}}_{\pi_{-1,\mathrm{H}}-\frac{1}{2},\pi_{-1,\mathrm{H}}-\frac{1}{2}}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle \\ & +\langle \pi_{-1,\mathrm{H}}-\tfrac{1}{2}|\hat{\mathrm{h}}|\pi_{-1,\mathrm{H}}-\tfrac{1}{2}\rangle+\sum_{\mathrm{p}}\langle \mathrm{p}|\hat{\mathscr{H}}_{\mathrm{D}}+\hat{V}_{\mathrm{DFE}}+\hat{V}_{\mathrm{CHDF}}|\mathrm{p}\rangle) \\ & -2\langle z_{\mathrm{H}}-\tfrac{1}{2}|\mathrm{v}-\tfrac{1}{2}\rangle\langle \mathrm{v}\tfrac{1}{2}|\hat{\mathrm{h}}+\hat{\mathrm{G}}_{\pi_{1,\mathrm{H}}\frac{1}{2},\pi_{1,\mathrm{H}}\frac{1}{2}}+\hat{\mathrm{G}}_{\pi_{-1,\mathrm{H}}-\frac{1}{2},\pi_{-1,\mathrm{H}}-\frac{1}{2}}|z_{\mathrm{H}}\tfrac{1}{2}\rangle \\ & +\langle z_{\mathrm{H}}-\tfrac{1}{2}|\hat{\mathrm{G}}_{\mathrm{v}\frac{1}{2},\mathrm{v}-\frac{1}{2}}|z_{\mathrm{H}}\tfrac{1}{2}\rangle+2\langle \pi_{-1,\mathrm{H}}-\tfrac{1}{2}|\mathrm{v}-\tfrac{1}{2}\rangle(\langle \mathrm{v}\tfrac{1}{2}|z_{\mathrm{H}}\tfrac{1}{2}\rangle\langle z_{\mathrm{H}}-\tfrac{1}{2}|\hat{\mathrm{h}} \\ & +\hat{\mathrm{G}}_{\pi_{1,\mathrm{H}}\frac{1}{2},\pi_{1,\mathrm{H}}\frac{1}{2}}|\pi_{-1,\mathrm{H}}-\tfrac{1}{2}\rangle+\langle z_{\mathrm{H}}-\tfrac{1}{2}|\hat{\mathrm{G}}_{\mathrm{v}\frac{1}{2},z\mathrm{H}\frac{1}{2}}|\pi_{-1,\mathrm{H}}-\tfrac{1}{2}\rangle) \\ & -\langle \pi_{-1,\mathrm{H}}-\tfrac{1}{2}|\mathrm{v}-\tfrac{1}{2}\rangle\langle \mathrm{v}\tfrac{1}{2}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle\langle \pi_{1,\mathrm{H}}\tfrac{1}{2}|\hat{\mathrm{G}}_{z\mathrm{H}-\frac{1}{2},\pi_{-1,\mathrm{H}}-\frac{1}{2}}|z_{\mathrm{H}}\tfrac{1}{2}\rangle,\end{aligned} \tag{6.11b}$$

by using both the relations (3.5) and the results

$$\left.\begin{aligned}\hat{\mathrm{H}}_{x,\mathrm{t}}|\pi_{\pm1,\mathrm{H}}\pm\tfrac{1}{2}\rangle &= \mathrm{i}|\pi_{\mp1,\mathrm{H}}\mp\tfrac{1}{2}\rangle, \\ \hat{\mathrm{H}}_{x,\mathrm{t}}|z_{\mathrm{H}}\pm\tfrac{1}{2}\rangle &= \mathrm{i}|z_{\mathrm{H}}\mp\tfrac{1}{2}\rangle,\end{aligned}\right\} \tag{6.12}$$

which are derived from (6.5) and (2.29). The results (6.9) and (6.11) show that the total energy ($E_{\mathrm{T}\kappa\mathrm{v}z}$), including internuclear repulsion, predicted by the wavefunction (6.7) is given by

$$\begin{aligned}E_{\mathrm{T}\kappa\mathrm{v}z} = {} & S^2\{S^{-2}(E_{\mathrm{CE}}+E_{\mathrm{CH}}+E_{\mathrm{CE-CH}})+(1-\langle \pi_{1,\mathrm{H}}\tfrac{1}{2}|\mathrm{v}\tfrac{1}{2}\rangle^2)(\langle \mathrm{p}_{\mathrm{H}}\tfrac{3}{2}|\hat{\mathscr{H}}_{\mathrm{D}}+\hat{V}_{\mathrm{DFE}}+\hat{V}_{\mathrm{CHDF}}|\mathrm{p}_{\mathrm{H}}\tfrac{3}{2}\rangle \\ & +\langle \mathrm{p}_{\mathrm{H}}-\tfrac{3}{2}|\hat{\mathscr{H}}_{\mathrm{D}}+\hat{V}_{\mathrm{DFE}}+\hat{V}_{\mathrm{CHDF}}|\mathrm{p}_{\mathrm{H}}-\tfrac{3}{2}\rangle+\langle \pi_{-1,\mathrm{H}}-\tfrac{1}{2}|\hat{\mathrm{h}}+\hat{\mathrm{G}}_{z\mathrm{H}-\frac{1}{2},z\mathrm{H}-\frac{1}{2}}|\pi_{-1,\mathrm{H}}-\tfrac{1}{2}\rangle \\ & +\langle z_{\mathrm{H}}-\tfrac{1}{2}|\hat{\mathrm{h}}|z_{\mathrm{H}}-\tfrac{1}{2}\rangle)+\langle \pi_{1,\mathrm{H}}\tfrac{1}{2}|\hat{\mathrm{h}}+\hat{\mathrm{G}}_{\pi_{-1,\mathrm{H}}-\frac{1}{2},\pi_{-1,\mathrm{H}}-\frac{1}{2}}+\hat{\mathrm{G}}_{z\mathrm{H}-\frac{1}{2},z\mathrm{H}-\frac{1}{2}}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle \\ & +\langle \mathrm{v}\tfrac{1}{2}|\hat{\mathrm{h}}+\hat{\mathrm{G}}_{\pi_{-1,\mathrm{H}}-\frac{1}{2},\pi_{-1,\mathrm{H}}-\frac{1}{2}}+\hat{\mathrm{G}}_{z\mathrm{H}-\frac{1}{2},z\mathrm{H}-\frac{1}{2}}|\mathrm{v}\tfrac{1}{2}\rangle-2\langle \mathrm{v}\tfrac{1}{2}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle\langle \pi_{1,\mathrm{H}}\tfrac{1}{2}|\hat{\mathrm{h}} \\ & +\hat{\mathrm{G}}_{\pi_{-1,\mathrm{H}}-\frac{1}{2},\pi_{-1,\mathrm{H}}-\frac{1}{2}}+\hat{\mathrm{G}}_{z\mathrm{H}-\frac{1}{2},z\mathrm{H}-\frac{1}{2}}|\mathrm{v}\tfrac{1}{2}\rangle+\langle \pi_{1,\mathrm{H}}\tfrac{1}{2}\mathrm{v}\tfrac{1}{2}|r_{12}^{-1}(1-\hat{\mathrm{P}}_{12})|\pi_{1,\mathrm{H}}\tfrac{1}{2}\mathrm{v}\tfrac{1}{2}\rangle \\ & \pm[-\langle z_{\mathrm{H}}-\tfrac{1}{2}|\mathrm{v}-\tfrac{1}{2}\rangle\langle \mathrm{v}\tfrac{1}{2}|z_{\mathrm{H}}\tfrac{1}{2}\rangle(\langle \mathrm{p}_{\mathrm{H}}\tfrac{3}{2}|\hat{\mathscr{H}}_{\mathrm{D}}+\hat{V}_{\mathrm{DFE}}+\hat{V}_{\mathrm{CHDF}}|\mathrm{p}_{\mathrm{H}}\tfrac{3}{2}\rangle \\ & +\langle \mathrm{p}_{\mathrm{H}}-\tfrac{3}{2}|\hat{\mathscr{H}}_{\mathrm{D}}+\hat{V}_{\mathrm{DFE}}+\hat{V}_{\mathrm{CHDF}}|\mathrm{p}_{\mathrm{H}}-\tfrac{3}{2}\rangle+\langle \pi_{1,\mathrm{H}}\tfrac{1}{2}|\hat{\mathrm{h}}+\hat{\mathrm{G}}_{\pi_{-1,\mathrm{H}}-\frac{1}{2},\pi_{-1,\mathrm{H}}-\frac{1}{2}}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle \\ & +\langle \pi_{-1,\mathrm{H}}-\tfrac{1}{2}|\hat{\mathrm{h}}|\pi_{-1,\mathrm{H}}-\tfrac{1}{2}\rangle)-2\langle z_{\mathrm{H}}-\tfrac{1}{2}|\mathrm{v}-\tfrac{1}{2}\rangle\langle \mathrm{v}\tfrac{1}{2}|\hat{\mathrm{h}}+\hat{\mathrm{G}}_{\pi_{1,\mathrm{H}}\frac{1}{2},\pi_{1,\mathrm{H}}\frac{1}{2}} \\ & +\hat{\mathrm{G}}_{\pi_{-1,\mathrm{H}}-\frac{1}{2},\pi_{-1,\mathrm{H}}-\frac{1}{2}}|z_{\mathrm{H}}\tfrac{1}{2}\rangle+\langle z_{\mathrm{H}}-\tfrac{1}{2}|\hat{\mathrm{G}}_{\mathrm{v}\frac{1}{2},\mathrm{v}-\frac{1}{2}}|z_{\mathrm{H}}\tfrac{1}{2}\rangle \\ & +2\langle \pi_{-1,\mathrm{H}}-\tfrac{1}{2}|\mathrm{v}-\tfrac{1}{2}\rangle(\langle \mathrm{v}\tfrac{1}{2}|z_{\mathrm{H}}\tfrac{1}{2}\rangle\langle z_{\mathrm{H}}-\tfrac{1}{2}|\hat{\mathrm{h}}+\hat{\mathrm{G}}_{\pi_{1,\mathrm{H}}\frac{1}{2},\pi_{1,\mathrm{H}}\frac{1}{2}}|\pi_{-1,\mathrm{H}}-\tfrac{1}{2}\rangle \\ & +\langle z_{\mathrm{H}}-\tfrac{1}{2}|\hat{\mathrm{G}}_{\mathrm{v}\frac{1}{2},z\mathrm{H}\frac{1}{2}}|\pi_{-1,\mathrm{H}}-\tfrac{1}{2}\rangle) \\ & -\langle \pi_{-1,\mathrm{H}}-\tfrac{1}{2}|\mathrm{v}-\tfrac{1}{2}\rangle\langle \mathrm{v}\tfrac{1}{2}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle\langle \pi_{1,\mathrm{H}}\tfrac{1}{2}|\hat{\mathrm{G}}_{z\mathrm{H}-\frac{1}{2},\pi_{-1,\mathrm{H}}-\frac{1}{2}}|z_{\mathrm{H}},\tfrac{1}{2}\rangle]\}+Z_{\mathrm{H}}Z_{\mathrm{E}}/R,\end{aligned} \tag{6.13}$$

with the normalization integral given by

$$S = (1-\langle \mathrm{v}\tfrac{1}{2}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle^2 \mp \langle z_{\mathrm{H}}-\tfrac{1}{2}|\mathrm{v}-\tfrac{1}{2}\rangle\langle \mathrm{v}\tfrac{1}{2}|z_{\mathrm{H}}\tfrac{1}{2}\rangle)^{-\frac{1}{2}}. \tag{6.14}$$

In (6.13), E_{CE} is the energy of the core of the element E in the absence of the halogen, E_{CH} is the corresponding energy of the halogen core while $E_{\mathrm{CE-CH}}$ is the energy of interaction between the two cores:

$$\left.\begin{aligned} E_{\mathrm{CE}} &= \sum_{\mathrm{c}} \langle \mathrm{c}|\hat{\mathscr{H}}_{\mathrm{k.e.}}+\hat{V}_{\mathrm{NE}}+\sum_{\mathrm{c}'<\mathrm{c}} \hat{\mathrm{G}}_{\mathrm{c}',\mathrm{c}'}|\mathrm{c}\rangle,\\ E_{\mathrm{CH}} &= \sum_{\mathrm{c_H}} \langle \mathrm{c_H}|\hat{\mathscr{H}}_{\mathrm{k.e.}}+\hat{V}_{\mathrm{NH}}+\sum_{\mathrm{c}'_{\mathrm{H}}<\mathrm{c_H}} \hat{\mathrm{G}}_{\mathrm{c}'_{\mathrm{H}},\mathrm{c}'_{\mathrm{H}}}|\mathrm{c_H}\rangle,\\ E_{\mathrm{CE-CH}} &= \sum_{\mathrm{c}} \langle \mathrm{c}|\hat{V}_{\mathrm{NH}}|\mathrm{c}\rangle+\sum_{\mathrm{c_H}} \langle \mathrm{c_H}|\hat{V}_{\mathrm{NE}}|\mathrm{c_H}\rangle+\sum_{\mathrm{cc_H}} \langle \mathrm{c}|\hat{\mathrm{G}}_{\mathrm{c_H},\mathrm{c_H}}|\mathrm{c}\rangle. \end{aligned}\right\} \tag{6.15}$$

The interaction energy cannot be immediately extracted from (6.13) because the halogen orbitals are eigenfunctions of a Fock operator constructed from the potential $\hat{V}_{\mathrm{NH}}+\hat{V}_{\mathrm{CHDF}}+\frac{4}{5}\hat{V}^{(0)}_{\mathrm{VH}}$ whereas the matrix element between $|\mathrm{v}\tfrac{1}{2}\rangle$ and $|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle$ in the fourth line of (6.13) and that between $|\mathrm{v}\tfrac{1}{2}\rangle$ and $|z_{\mathrm{H}}\tfrac{1}{2}\rangle$ in the eighth line are both taken over slightly different potentials, However, the Dirac–Fock equation (6.4) enables these matrix elements to be simplified because it shows that

$$\begin{aligned} &\langle \mathrm{v}\tfrac{1}{2}|\hat{\mathscr{H}}_{\mathrm{k.e.}}+\hat{V}_{\mathrm{NH}}+\hat{V}_{\mathrm{CHDF}}+\hat{\mathrm{G}}_1|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle\\ &\quad= \langle \mathrm{v}\tfrac{1}{2}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle\epsilon_{\mathrm{w}}+\langle \mathrm{v}\tfrac{1}{2}|\tfrac{1}{5}\hat{\mathrm{G}}_1-\tfrac{4}{5}\hat{\mathrm{G}}_{z\mathrm{H}\frac{1}{2},z\mathrm{H}\frac{1}{2}}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle\\ &\quad= \langle \mathrm{v}\tfrac{1}{2}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle\langle\pi_{1,\mathrm{H}}\tfrac{1}{2}|\hat{\mathscr{H}}_{\mathrm{k.e.}}+\hat{V}_{\mathrm{NH}}+\hat{V}_{\mathrm{CHDF}}+\hat{\mathrm{G}}_1|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle+\langle \mathrm{v}\tfrac{1}{2}|\tfrac{1}{5}\hat{\mathrm{G}}_1-\tfrac{4}{5}\hat{\mathrm{G}}_{z\mathrm{H}\frac{1}{2},z\mathrm{H}\frac{1}{2}}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle\\ &\qquad-\langle \mathrm{v}\tfrac{1}{2}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle\langle\pi_{1,\mathrm{H}}\tfrac{1}{2}|\tfrac{1}{5}\hat{\mathrm{G}}_1-\tfrac{4}{5}\hat{\mathrm{G}}_{z\mathrm{H}\frac{1}{2},z\mathrm{H}\frac{1}{2}}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle, \end{aligned} \tag{6.16a}$$

$$\begin{aligned} &\langle \mathrm{v}\tfrac{1}{2}|\hat{\mathscr{H}}_{\mathrm{k.e.}}+\hat{V}_{\mathrm{NH}}+\hat{V}_{\mathrm{CHDF}}+\hat{\mathrm{G}}_2|z_{\mathrm{H}}\tfrac{1}{2}\rangle\\ &\quad= \langle \mathrm{v}\tfrac{1}{2}|z_{\mathrm{H}}\tfrac{1}{2}\rangle\epsilon_{\mathrm{w}}+\langle \mathrm{v}\tfrac{1}{2}|\tfrac{1}{5}\hat{\mathrm{G}}_2-\tfrac{4}{5}\hat{\mathrm{G}}_{z\mathrm{H}-\frac{1}{2},z\mathrm{H}-\frac{1}{2}}|z_{\mathrm{H}}\tfrac{1}{2}\rangle\\ &\quad= \langle \mathrm{v}\tfrac{1}{2}|z_{\mathrm{H}}\tfrac{1}{2}\rangle\langle z_{\mathrm{H}}\tfrac{1}{2}|\hat{\mathscr{H}}_{\mathrm{k.e.}}+\hat{V}_{\mathrm{NH}}+\hat{V}_{\mathrm{CHDF}}+\hat{\mathrm{G}}_2|\mathrm{v}\tfrac{1}{2}\rangle+\langle \mathrm{v}\tfrac{1}{2}|\tfrac{1}{5}\hat{\mathrm{G}}_2-\tfrac{4}{5}\hat{\mathrm{G}}_{z\mathrm{H}-\frac{1}{2},z\mathrm{H}-\frac{1}{2}}|z_{\mathrm{H}}\tfrac{1}{2}\rangle\\ &\qquad-\langle \mathrm{v}\tfrac{1}{2}|z_{\mathrm{H}}\tfrac{1}{2}\rangle\langle z_{\mathrm{H}}\tfrac{1}{2}|\tfrac{1}{5}\hat{\mathrm{G}}_2-\tfrac{4}{5}\hat{\mathrm{G}}_{z\mathrm{H}-\frac{1}{2},z\mathrm{H}-\frac{1}{2}}|z_{\mathrm{H}}\tfrac{1}{2}\rangle, \end{aligned} \tag{6.16b}$$

$$\langle z_{\mathrm{H}}-\tfrac{1}{2}|\hat{\mathscr{H}}_{\mathrm{k.e.}}+\hat{V}_{\mathrm{NH}}+\hat{V}_{\mathrm{CHDF}}+\hat{\mathrm{G}}_3|\pi_{-1,\mathrm{H}}-\tfrac{1}{2}\rangle = \langle z_{\mathrm{H}}-\tfrac{1}{2}|\tfrac{1}{5}\hat{\mathrm{G}}_3-\tfrac{4}{5}\hat{\mathrm{G}}_{z\mathrm{H}\frac{1}{2},z\mathrm{H}\frac{1}{2}}|\pi_{-1,\mathrm{H}}-\tfrac{1}{2}\rangle, \tag{6.16c}$$

where

$$\hat{\mathrm{G}}_1 = \hat{\mathrm{G}}_{\mathrm{pH}\frac{3}{2},\mathrm{pH}\frac{3}{2}}+\hat{\mathrm{G}}_{\mathrm{pH}-\frac{3}{2},\mathrm{pH}-\frac{3}{2}}+\hat{\mathrm{G}}_{\pi_{-1,\mathrm{H}}-\frac{1}{2},\pi_{-1,\mathrm{H}}-\frac{1}{2}}+\hat{\mathrm{G}}_{z\mathrm{H}-\frac{1}{2},z\mathrm{H}-\frac{1}{2}}, \tag{6.17a}$$

$$\hat{\mathrm{G}}_2 = \hat{\mathrm{G}}_{\mathrm{pH}\frac{3}{2},\mathrm{pH}\frac{3}{2}}+\hat{\mathrm{G}}_{\mathrm{pH}-\frac{3}{2},\mathrm{pH}-\frac{3}{2}}+\hat{\mathrm{G}}_{\pi_{1,\mathrm{H}}\frac{1}{2},\pi_{1,\mathrm{H}}\frac{1}{2}}+\hat{\mathrm{G}}_{\pi_{-1,\mathrm{H}}-\frac{1}{2},\pi_{-1,\mathrm{H}}-\frac{1}{2}}, \tag{6.17b}$$

$$\hat{\mathrm{G}}_3 = \hat{\mathrm{G}}_{\mathrm{pH}\frac{3}{2},\mathrm{pH}\frac{3}{2}}+\hat{\mathrm{G}}_{\mathrm{pH}-\frac{3}{2},\mathrm{pH}-\frac{3}{2}}+\hat{\mathrm{G}}_{\pi_1\,\mathrm{H}\frac{1}{2},\pi_{1,\mathrm{H}}\frac{1}{2}}. \tag{6.17c}$$

In (6.16*c*) the orthogonality of the halogen orbitals causes the term involving the orbital energy ϵ_{w} to vanish. After noting that the energy (E_{hal}) of the free halogen is given by

$$E_{\mathrm{hal}} = E_{\mathrm{CH}}+\sum_{\mathrm{w}}\langle \mathrm{w}|\hat{\mathscr{H}}_{\mathrm{k.e.}}+\hat{V}_{\mathrm{NH}}+\hat{V}_{\mathrm{CHDF}}|\mathrm{w}\rangle+\sum_{\mathrm{w}'<\mathrm{w}}\langle \mathrm{w}|\hat{\mathrm{G}}_{\mathrm{w}',\mathrm{w}'}|\mathrm{w}\rangle$$

$$(\mathrm{w} = \mathrm{p_H}\tfrac{3}{2},\ \mathrm{p_H}-\tfrac{3}{2},\ \pi_{1,\mathrm{H}}\tfrac{1}{2},\ \pi_{-1,\mathrm{H}}-\tfrac{1}{2},\ z_{\mathrm{H}}\tfrac{1}{2}) \tag{6.18}$$

and invoking the relations (cf. §3(*a*), stage 2)

$$\left.\begin{aligned} \sum_{\mathrm{c}}\langle \mathrm{c}|\hat{V}_{\mathrm{NH}}+\hat{V}_{\mathrm{CHDF}}|\mathrm{c}\rangle &= -5(Z_{\mathrm{E}}-1)/R,\\ \sum_{\mathrm{c_H}}\langle \mathrm{c_H}|\hat{V}_{\mathrm{NE}}+\hat{V}_{\mathrm{DFE}}|\mathrm{c_H}\rangle &= -(Z_{\mathrm{H}}-5)/R, \end{aligned}\right\} \tag{6.19}$$

substitution of the relations (6.16) in (6.13) shows that the interaction energy predicted by (6.7) is

$$
\begin{aligned}
E_{\mathrm{int}}(\kappa\mathrm{v}z) = {} & \langle \mathrm{p_H}\tfrac{3}{2}|\hat{V}_{\mathrm{TE}}|\mathrm{p_H}\tfrac{3}{2}\rangle + \langle \mathrm{p_H}-\tfrac{3}{2}|\hat{V}_{\mathrm{TE}}|\mathrm{p_H}-\tfrac{3}{2}\rangle + \langle \pi_{-1,\mathrm{H}}-\tfrac{1}{2}|\hat{V}_{\mathrm{TE}}|\pi_{-1,\mathrm{H}}-\tfrac{1}{2}\rangle + 3R^{-1} \\
& + S^2\{\langle \mathrm{v}\tfrac{1}{2}|\hat{V}_{\mathrm{NH}}+\hat{V}_{\mathrm{CHDF}}+\hat{\mathrm{G}}_1+\hat{\mathrm{G}}_{\pi_{1,\mathrm{H}}\frac{1}{2},\,\pi_{1,\mathrm{H}}\frac{1}{2}}|\mathrm{v}\tfrac{1}{2}\rangle \\
& + (1\mp\langle z_{\mathrm{H}}-\tfrac{1}{2}|\mathrm{v}-\tfrac{1}{2}\rangle\langle \mathrm{v}\tfrac{1}{2}|z_{\mathrm{H}}\tfrac{1}{2}\rangle)(\langle \pi_{1,\mathrm{H}}\tfrac{1}{2}|\hat{V}_{\mathrm{TE}}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle + R^{-1}) - \langle \pi_{1,\mathrm{H}}\tfrac{1}{2}|\mathrm{v}\tfrac{1}{2}\rangle \\
& \times (\langle \mathrm{v}\tfrac{1}{2}|\hat{V}_{\mathrm{TE}}+\hat{V}_{\mathrm{NH}}+\hat{V}_{\mathrm{CHDF}}+\hat{\mathrm{G}}_1|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle + \langle \pi_{1,\mathrm{H}}\tfrac{1}{2}|\mathrm{v}\tfrac{1}{2}\rangle R^{-1}) + (1-\langle \pi_{1,\mathrm{H}}\tfrac{1}{2}|\mathrm{v}\tfrac{1}{2}\rangle^2) \\
& \times (\langle z_{\mathrm{H}}-\tfrac{1}{2}|\hat{V}_{\mathrm{TE}}|z_{\mathrm{H}}-\tfrac{1}{2}\rangle + R^{-1}) \mp \langle z_{\mathrm{H}}-\tfrac{1}{2}|\mathrm{v}-\tfrac{1}{2}\rangle \\
& \times (\langle \mathrm{v}\tfrac{1}{2}|\hat{V}_{\mathrm{TE}}+\hat{V}_{\mathrm{NH}}+\hat{V}_{\mathrm{CHDF}}+\hat{\mathrm{G}}_2|z_{\mathrm{H}}\tfrac{1}{2}\rangle + \langle \mathrm{v}\tfrac{1}{2}|z_{\mathrm{H}}\tfrac{1}{2}\rangle R^{-1}) \pm \langle z_{\mathrm{H}}-\tfrac{1}{2}|\hat{\mathrm{G}}_{\mathrm{v}\frac{1}{2},\,\mathrm{v}-\frac{1}{2}}|z_{\mathrm{H}}\tfrac{1}{2}\rangle \\
& \pm 2\langle \pi_{-1,\mathrm{H}}-\tfrac{1}{2}|\mathrm{v}-\tfrac{1}{2}\rangle(\langle \mathrm{v}\tfrac{1}{2}|z_{\mathrm{H}}\tfrac{1}{2}\rangle\langle z_{\mathrm{H}}-\tfrac{1}{2}|\hat{V}_{\mathrm{TE}}|\pi_{-1,\mathrm{H}}-\tfrac{1}{2}\rangle \\
& + \langle z_{\mathrm{H}}-\tfrac{1}{2}|\hat{\mathrm{G}}_{\mathrm{v}\frac{1}{2},\,z_{\mathrm{H}}\frac{1}{2}}|\pi_{-1,\mathrm{H}}-\tfrac{1}{2}\rangle) \mp \langle \pi_{-1,\mathrm{H}}-\tfrac{1}{2}|\mathrm{v}-\tfrac{1}{2}\rangle \\
& \times \langle \mathrm{v}\tfrac{1}{2}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle\langle \pi_{1,\mathrm{H}}\tfrac{1}{2}|\hat{\mathrm{G}}_{z_{\mathrm{H}}-\frac{1}{2},\,\pi_{-1,\mathrm{H}}-\frac{1}{2}}|z_{\mathrm{H}}\tfrac{1}{2}\rangle - R_1 \mp R_2 \pm 2R_3\},
\end{aligned} \qquad (6.20a)
$$

with

$$\hat{V}_{\mathrm{TE}} = \hat{V}_{\mathrm{NE}} + \hat{V}_{\mathrm{DFE}}. \qquad (6.20b)$$

In (6.20*a*) the quantities R_1, R_2 and R_3, which are closely related to terms appearing in (6.16), are defined through

$$
\begin{aligned}
R_1 = {} & \langle \pi_{1,\mathrm{H}}\tfrac{1}{2}|\mathrm{v}\tfrac{1}{2}\rangle(\langle \mathrm{v}\tfrac{1}{2}|\tfrac{1}{5}\hat{\mathrm{G}}_1-\tfrac{4}{5}\hat{\mathrm{G}}_{z_{\mathrm{H}}\frac{1}{2},\,z_{\mathrm{H}}\frac{1}{2}}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle \\
& - \langle \mathrm{v}\tfrac{1}{2}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle\langle \pi_{1,\mathrm{H}}\tfrac{1}{2}|\tfrac{1}{5}\hat{\mathrm{G}}_1-\tfrac{4}{5}\hat{\mathrm{G}}_{z_{\mathrm{H}}\frac{1}{2},\,z_{\mathrm{H}}\frac{1}{2}}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle,
\end{aligned} \qquad (6.21a)
$$

$$
\begin{aligned}
R_2 = {} & \langle z_{\mathrm{H}}-\tfrac{1}{2}|\mathrm{v}-\tfrac{1}{2}\rangle(\langle \mathrm{v}\tfrac{1}{2}|\tfrac{1}{5}\hat{\mathrm{G}}_2-\tfrac{4}{5}\hat{\mathrm{G}}_{z_{\mathrm{H}}-\frac{1}{2},\,z_{\mathrm{H}}-\frac{1}{2}}|z_{\mathrm{H}}\tfrac{1}{2}\rangle \\
& - \langle \mathrm{v}\tfrac{1}{2}|z_{\mathrm{H}}\tfrac{1}{2}\rangle\langle z_{\mathrm{H}}\tfrac{1}{2}|\tfrac{1}{5}\hat{\mathrm{G}}_2-\tfrac{4}{5}\hat{\mathrm{G}}_{z_{\mathrm{H}}-\frac{1}{2},\,z_{\mathrm{H}}-\frac{1}{2}}|z_{\mathrm{H}}\tfrac{1}{2}\rangle,
\end{aligned} \qquad (6.21b)
$$

$$R_3 = \langle \pi_{-1,\mathrm{H}}-\tfrac{1}{2}|\mathrm{v}-\tfrac{1}{2}\rangle\langle \mathrm{v}\tfrac{1}{2}|z_{\mathrm{H}}\tfrac{1}{2}\rangle\langle z_{\mathrm{H}}-\tfrac{1}{2}|\tfrac{1}{5}\hat{\mathrm{G}}_1-\tfrac{4}{5}\hat{\mathrm{G}}_{z_{\mathrm{H}}\frac{1}{2},\,z_{\mathrm{H}}\frac{1}{2}}|\pi_{-1,\mathrm{H}}-\tfrac{1}{2}\rangle. \qquad (6.21c)$$

In the last two steps of the four-step process of investigating the bonding described by the wavefunction (6.7) the expression obtained by approximating (6.20*a*) by the terms containing only large components is compared with the interaction energies predicted by non-relativistic wavefunctions of known bonding characteristics. It is therefore useful to introduce the non-relativistic wavefunctions

$$|{}^{1,\mathrm{N}}\mathrm{ab}\mu\mu'\rangle = S\hat{\mathscr{A}}(|\mathrm{core}_{\mu}^{\mathrm{NR}}\rangle|\mathrm{core}_{\mu'}^{\mathrm{NR}}\rangle|\mathrm{a}_{\mu}^{\mathrm{NR}}\mathrm{b}_{\mu'}^{\mathrm{NR}}\rangle\tfrac{1}{\sqrt{2}}|\alpha\beta-\beta\alpha\rangle), \qquad (6.22)$$

$$|{}^{3}\mathrm{ab}\mu\mu'\rangle = S\hat{\mathscr{A}}(|\mathrm{core}_{\mu}^{\mathrm{NR}}\rangle|\mathrm{core}_{\mu'}^{\mathrm{NR}}\rangle|\mathrm{a}_{\mu}^{\mathrm{NR}}\mathrm{b}_{\mu'}^{\mathrm{NR}}\rangle|\alpha\alpha\rangle), \qquad (6.23)$$

which describe the interaction of atom μ containing a single unpaired electron occupying spatial orbital $|\mathrm{a}_{\mu}^{\mathrm{NR}}\rangle$ with atom μ' containing an unpaired electron in spatial orbital $|\mathrm{b}_{\mu'}^{\mathrm{NR}}\rangle$ The spins of the valence electrons are coupled to form a singlet state in (6.22) while they are parallel in (6.23). The quantity $|\mathrm{core}_{\mu}^{\mathrm{NR}}\rangle$ is a Hartree product constructed from the non-relativistic core orbitals of atom μ (cf. (6.8)) while the orbitals $|\mathrm{a}_{\mu}^{\mathrm{NR}}\rangle$ and $|\mathrm{b}_{\mu'}^{\mathrm{NR}}\rangle$ satisfy the non-relativistic atomic Hartree–Fock equations

$$
\left.
\begin{aligned}
(\tfrac{1}{2}\hat{\mathrm{p}}^2+\hat{V}_{\mu})\,|\mathrm{a}_{\mu}^{\mathrm{NR}}\rangle &= \epsilon_{\mathrm{a}\mu}^{\mathrm{NR}}|\mathrm{a}_{\mu}^{\mathrm{NR}}\rangle + \sum_{\mathrm{c}_{\mu}} \epsilon_{\mathrm{c}_{\mu}\mathrm{a}_{\mu}}|\mathrm{c}_{\mu}^{\mathrm{NR}}\rangle, \\
(\tfrac{1}{2}\hat{\mathrm{p}}^2+\hat{V}_{\mu'})\,|\mathrm{b}_{\mathrm{b}\mu'}^{\mathrm{NR}}\rangle &= \epsilon_{\mu'}^{\mathrm{NR}}|\mathrm{b}_{\mu'}^{\mathrm{NR}}\rangle + \sum_{\mathrm{c}_{\mu'}} \epsilon_{\mathrm{c}_{\mu'}\mathrm{b}_{\mu'}}|\mathrm{c}_{\mu'}^{\mathrm{NR}}\rangle,
\end{aligned}
\right\} \qquad (6.24)
$$

where the potential $\hat{V}_\mu$ consists of the nuclear attraction plus the direct and exchange potentials constructed from the core orbitals of atom μ. The interaction energies predicted by (6.22) and (6.23) respectively are, under the standard orthogonality assumptions,

$$E_{\text{int}}({}^{1,\text{N}}\text{ab}\mu\mu') = (1+\langle \text{a}_\mu^{\text{NR}}|\text{b}_{\mu'}^{\text{NR}}\rangle^2)^{-1}\;{}^{1,\text{N}}H_{\text{int}}(\text{a}_\mu^{\text{NR}}, \text{b}_{\mu'}^{\text{NR}}, V_\mu, V_{\mu'}), \tag{6.25a}$$

$$E_{\text{int}}({}^3\text{ab}\mu\mu') = (1-\langle \text{a}_\mu^{\text{NR}}|\text{b}_{\mu'}^{\text{NR}}\rangle^2)^{-1}\;{}^{3,\text{N}}H_{\text{int}}(\text{a}_\mu^{\text{NR}}, \text{b}_{\mu'}^{\text{NR}}, V_\mu, V_{\mu'}), \tag{6.25b}$$

where

$$\begin{aligned}{}^{1,\text{N}}H_{\text{int}}(\text{a}, \text{b}, \hat{V}_\mu, \hat{V}_{\mu'}) = {} & \langle \text{a}|\hat{V}_{\mu'}|\text{a}\rangle + \langle \text{b}|\hat{V}_\mu|\text{b}\rangle + \langle \text{ab}|r_{12}^{-1}|\text{ab}\rangle + R^{-1} \\ & + \langle \text{a}|\text{b}\rangle\langle \text{b}|\hat{V}_\mu + \hat{V}_{\mu'} + R^{-1}|\text{a}\rangle + \langle \text{ab}|r_{12}^{-1}|\text{ba}\rangle,\end{aligned} \tag{6.26a}$$

$$\begin{aligned}{}^{3,\text{N}}H_{\text{int}}(\text{a}, \text{b}, \hat{V}_\mu, \hat{V}_{\mu'}) = {} & \langle \text{a}|\hat{V}_{\mu'}|\text{a}\rangle + \langle \text{b}|\hat{V}_\mu|\text{b}\rangle + \langle \text{ab}|r_{12}^{-1}|\text{ab}\rangle + R^{-1} \\ & - \langle \text{a}|\text{b}\rangle\langle \text{b}|\hat{V}_\mu + \hat{V}_{\mu'} + R^{-1}|\text{a}\rangle - \langle \text{ab}|r_{12}^{-1}|\text{ba}\rangle.\end{aligned} \tag{6.26b}$$

The superscripts 1 and 3 in (6.26) denote that these quantities are associated with singlet, (6.22), and triplet, (6.23), wavefunctions respectively, while the further superscript N denotes that the valence orbitals a, b are in general non-orthogonal. In the special case of (6.23) in which the orbitals $|\text{a}_\mu^{\text{NR}}\rangle$ and $|\text{b}_{\mu'}^{\text{NR}}\rangle$ are orthogonal, the interaction energy (6.26*b*) becomes

$$E_{\text{int}}({}^3\text{ab}\mu\mu') = {}^{3,0}H_{\text{int}}(\text{a}_\mu^{\text{NR}}, \text{b}_{\mu'}^{\text{NR}}, V_\mu, V_{\mu'}) \tag{6.27}$$

with

$${}^{3,0}H_{\text{int}}(\text{a}, \text{b}, V_\mu, V_{\mu'}) = \langle \text{a}|\hat{V}_{\mu'}|\text{a}\rangle + \langle \text{b}|\hat{V}_\mu|\text{b}\rangle + \langle \text{ab}|r_{12}^{-1}|\text{ab}\rangle + R^{-1} - \langle \text{ab}|r_{12}^{-1}|\text{ba}\rangle. \tag{6.28}$$

The superscript 0 in (6.28) denotes that this function only yields the interaction energy when the orbitals $|\text{a}\rangle$ and $|\text{b}\rangle$ do not overlap. Substituting the large components (3.9) into (6.20) and expressing the result in terms of (6.26) show that the interaction energy predicted by (6.7) is

$$\begin{aligned}E_{\text{int}}(\kappa v z) = {} & [1+\text{a}\langle \text{p}_{0,\text{H}}|\text{p}_0\rangle^2 - (1-\text{a})\,\langle \text{p}_{1,\text{H}}|\text{p}_1\rangle^2]^{-1}\{a[{}^{1,\text{N}}H_{\text{int}}(\text{p}_0, \text{p}_{0,\text{H}}, \hat{V}_\text{E}, \hat{V}_{z,\text{H}}) \\ & + {}^1X_{\text{el}}(\text{p}_0, \text{p}_{1,\text{H}}, \text{p}_{-1,\text{H}}, \text{p}_{0,\text{H}})] + (1-a)\,[{}^{3,\text{N}}H_{\text{int}}(\text{p}_1, \text{p}_{1,\text{H}}, \hat{V}_\text{E}, \hat{V}_{1,\text{H}}) \\ & + {}^3X_{\text{el}}(\text{p}_1, \text{p}_{0,\text{H}}, \text{p}_{-1,\text{H}}, \text{p}_{1,\text{H}})] + [a\langle \text{p}_{0,\text{H}}|\text{p}_0\rangle^2\,(\langle \text{p}_{1,\text{H}}|\hat{V}_\text{E}|\text{p}_{1,\text{H}}\rangle + R^{-1}) \\ & - (1-a)\,\langle \text{p}_{1,\text{H}}|\text{p}_1\rangle^2\,(\langle \text{p}_{0,\text{H}}|\hat{V}_\text{E}|\text{p}_{0,\text{H}}\rangle + R^{-1})] + a\langle \text{p}_{1,\text{H}}|\hat{V}_\text{E}|\text{p}_{1,\text{H}}\rangle \\ & + (1-a)\,\langle \text{p}_{0,\text{H}}|\hat{V}_\text{E}|\text{p}_{0,\text{H}}\rangle + R^{-1} + R_1 + R_2\} + 3(\langle \text{p}_{1,\text{H}}|\hat{V}_\text{E}|\text{p}_{1.\text{H}}\rangle + R^{-1})\end{aligned} \tag{6.29}$$

where†

$$\left.\begin{aligned}{}^1X_{\text{el}}(d, e, \text{f}, \text{g}) &= -\langle d|\hat{\text{K}}_\text{e} + \hat{\text{K}}_\text{f}|d\rangle - \langle d|\text{g}\rangle\langle \text{g}|\hat{\text{K}}_\text{e} + \hat{\text{K}}_\text{f}|d\rangle, \\ {}^3X_{\text{el}}(d, e, \text{f}, \text{g}) &= -\langle d|\hat{\text{K}}_\text{e} + \hat{\text{K}}_\text{f}|d\rangle + \langle d|\text{g}\rangle\langle \text{g}|\hat{\text{K}}_\text{e} + \hat{\text{K}}_\text{f}|d\rangle,\end{aligned}\right\} \tag{6.30}$$

$$\left.\begin{aligned}\hat{V}_{z,\text{H}} &= \hat{V}_{\text{NH}} + \hat{V}'_{\text{CHDF}} + 2(\hat{\text{J}}_{\text{p}_{1,\text{H}}} + \hat{\text{J}}_{\text{p}_{-1,\text{H}}}), \\ \hat{V}_{1,\text{H}} &= \hat{V}_{\text{NH}} + \hat{V}'_{\text{CHDF}} + \hat{\text{J}}_{\text{p}_{1,\text{H}}} + \hat{\text{J}}_{\text{p}_{0,\text{H}}} + 2\hat{\text{J}}_{\text{p}_{-1,\text{H}}}.\end{aligned}\right\} \tag{6.31}$$

Here $\hat{V}'_{\text{CHDF}}$, with matrix elements defined by (3.10*d*), is the sum of the local potential generated by the full relativistic halogen core (6.8) plus the exchange potential generated by the core large components. In (6.20) the terms in square brackets and R_3 vanish if only the large components are considered.

Interpretation of the result (6.29) is simplified by noting that each of the terms in the fourth pair of square brackets is negligible because it just consists of part of a Heitler–London coulomb interaction multiplied by the square of an overlap, while it is shown in Appendix 6 that the terms R_1 and R_2 are negligible. The terms R_1 and R_2 would not be expected to constitute more than a small fraction of the interaction energy because they only arise through the difference

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† The definition of $\hat{V}_{1,\text{H}}$, (6.31), corrects that presented in Pyper (1980*b*).

between the potential $\frac{4}{5}\hat{V}^{(0)}_{\mathrm{VH}}$ generated by the average of the six states $\mathrm{w}_{\mathrm{vac}}$ and that arising from the $\pi^4\mathrm{p}_z$ valence state. This difference only enters the calculation because the halogen valence orbitals are taken to be symmetry adapted. The factors, a multiplying ${}^{1,\mathrm{N}}H_{\mathrm{int}}(\mathrm{p}_0, \mathrm{p}_{0,\mathrm{H}}, V_{\mathrm{E}}, V_{z,\mathrm{H}})$, and $(1-a)$ multiplying ${}^{3,\mathrm{N}}H_{\mathrm{int}}(\mathrm{p}_1, \mathrm{p}_{1,\mathrm{H}}, V_{\mathrm{E}}, V_{1,\mathrm{H}})$ in (6.29), show that in the small-overlap limit the $\bar{\mathrm{p}}$–Hal bond described by the wavefunction (6.7) is $\frac{1}{3}$ non-orthogonal Heitler–London singlet bonding and $\frac{2}{3}$ non-orthogonal Heitler–London triplet anti-bonding and that these proportions are reversed for the p–Hal bond, (6.7). The non-orthogonal singlet fractions are readily understood by realizing that the Kappa valence bond formed between the valence orbital $|\mathrm{v}\tfrac{1}{2}\rangle$ and an orbital whose large components have pure σ spatial symmetry is, for the $\bar{\mathrm{p}}$ and p cases respectively, $\frac{1}{3}$ and $\frac{2}{3}$ non-orthogonal Heitler–London singlet in character essentially because the large components of the orbitals $|\mathrm{v} \pm \tfrac{1}{2}\rangle$ have $\frac{1}{3}$ and $\frac{2}{3}\sigma$ character. The destabilizing non-orthogonal triplet contribution arises from the overlap of the orbitals $|\mathrm{v} \pm \tfrac{1}{2}\rangle$ with the halogen orbitals $|\pi_{\pm 1,\mathrm{H}} \pm \tfrac{1}{2}\rangle$, not participating in the Kappa valence bond, whose large components have the same spatial symmetry and spin as those of $|\mathrm{v} \pm \tfrac{1}{2}\rangle$. The fractions $\frac{2}{3}$ and $\frac{1}{3}$ in the $\bar{\mathrm{p}}$ and p cases respectively arise simply because the large components of the orbitals $|\mathrm{v} \pm \tfrac{1}{2}\rangle$ are $\frac{2}{3}$ and $\frac{1}{3}\pi$ in character. The two terms ${}^{1}X_{\mathrm{el}}(\mathrm{p}_0, \mathrm{p}_{1,\mathrm{H}}, \mathrm{p}_{-1,\mathrm{H}}, \mathrm{p}_{0,\mathrm{H}})$ and ${}^{3}X_{\mathrm{el}}(\mathrm{p}_1, \mathrm{p}_{0,\mathrm{H}}, \mathrm{p}_{-1,\mathrm{H}}, \mathrm{p}_{1,\mathrm{H}})$ can be simply interpreted as the exchange corrections to the purely local potentials entering ${}^{1,\mathrm{N}}H_{\mathrm{int}}(\mathrm{p}_0, \mathrm{p}_{0,\mathrm{H}}, V_{\mathrm{E}}, V_{z,\mathrm{H}})$ and ${}^{3,\mathrm{N}}H_{\mathrm{int}}(\mathrm{p}_1, \mathrm{p}_{1,\mathrm{H}}, V_{\mathrm{E}}, V_{1,\mathrm{H}})$ respectively. Hence if the four terms of the type $\langle \mathrm{p}_{m,\mathrm{H}}|\hat{V}_{\mathrm{E}}|\mathrm{p}_{m,\mathrm{H}}\rangle + R^{-1}$ are neglected, the orders of the $\bar{\mathrm{p}}$–Hal and p–Hal bonds described by (6.7) are $-\frac{1}{3}$ and $\frac{1}{3}$ in the limit of small overlaps $|\langle \mathrm{p}_{0,\mathrm{H}}|\mathrm{p}_0\rangle|$ and $\langle \mathrm{p}_{1,\mathrm{H}}|\mathrm{p}_1\rangle$ if the orders of non-orthogonal Heitler–London singlet and triplet bonds are taken to be 1 and -1 respectively. The actual orders will be slightly greater than $-\frac{1}{3}$ and $\frac{1}{3}$ because the terms $\langle \mathrm{p}_{m,\mathrm{H}}|\hat{V}_{\mathrm{E}}|\mathrm{p}_{m,\mathrm{H}}\rangle + R^{-1}$ will not be negligible. The presence of the destabilizing non-orthogonal triplet contribution to the interaction energy (6.29) shows that bonding modes different from that described by the wavefunction (6.7) need to be examined.

The results of the last paragraph do not in fact apply to the covalent bond formed between a halogen and a heavy element containing a single $\bar{\mathrm{p}}$ or p valence electron because the degeneracy in the free atom of the halogen orbitals differing only in the m_j quantum number permits the existence of a bonding mode different from that described by (6.7). However, these results do apply to the interaction of such a heavy element with a group described in non-relativistic theory as containing four π electrons and one σ electron for which the π–σ energy separation is large. The interaction energy for such a system, which is still described by a wavefunction of the type (6.7), is again given by (6.29) except that the terms R_1 and R_2 are not present because the orbitals $|\pi_{1,\mathrm{H}} \pm \tfrac{1}{2}\rangle$ and $|\mathrm{z}_{\mathrm{H}} \pm \tfrac{1}{2}\rangle$ are now eigenfunctions of the Fock hamiltonian for the isolated group. The prediction of a negative bond order $(-\frac{1}{3})$ shows that the interaction of such a group with a heavy element containing a single $\bar{\mathrm{p}}$ valence electron will not lead to the formation of a covalent bond having the length and strength usually associated with such a bond. However, since the attractive contribution to such an interaction arises from the overlap of σ orbitals while the repulsive one arises from that of π orbitals, one cannot conclude that the potential energy curve for such a system will be purely repulsive. One therefore predicts that there will be a very shallow minimum whose binding energy is much less than that of a normal covalent bond at a large internuclear separation, but that the interaction will be purely repulsive at internuclear distances corresponding to those of normal covalent bonds. The prediction of a bond order of $\frac{1}{3}$ shows that the bond between such a group and a heavy element containing a single valence p electron will not be as weak as for the $\bar{p}$ case although the presence of the π anti-bonding component does mean that the former bond will be very significantly weakened compared with a normal covalent bond.

It should be pointed out that the basic qualitative conclusions of this section do not change even if the σ bonding orbital of the halogen is some sp hybrid rather than being pure p_z.

(ii) *Interaction with the optimum halogen valence state*

A halogen in interaction with an element or group described in non-relativistic theory as containing a single unpaired electron in a σ orbital does not remain in its ground $\bar{p}_H^2 p_H^3$ configuration. It adopts instead the $\pi^4 p_z$ valence state, which is a linear combination of the $\bar{p}_H^2 p_H^3$ and the excited $\bar{p}_H p_H^4$ configurations, because this maximizes the overlap with the orbital of the other group thus leading to the formation of a strong bond. It is shown elsewhere (paper III) that for all the halogens except Astatine the excitation energies to the $\pi^4 p_z$ valence states are negligible compared with chemical bond energies so that the optimal valence states are essentially pure $\pi^4 p_z$. Similar reasoning shows that a halogen in interaction with a heavy element containing a single valence $\bar{p}$ or p electron will adopt that valence state which yields the strongest bond and that there is no reason for supposing that this valence state is $\pi^4 p_z$. It is therefore useful to introduce halogen bonding orbitals $|b_H \pm \tfrac{1}{2}\rangle$ and non-bonding orbitals $|n_H \pm \tfrac{1}{2}\rangle$ as linear combinations of the functions (6.5):

$$\left.\begin{aligned} |b_H \pm \tfrac{1}{2}\rangle &= -t_\sigma|\pi_{\pm 1,\mathrm{H}} \pm \tfrac{1}{2}\rangle + t_\pi|z_H \pm \tfrac{1}{2}\rangle, \\ |n_H \pm \tfrac{1}{2}\rangle &= t_\pi|\pi_{\pm 1,\mathrm{H}} \pm \tfrac{1}{2}\rangle + t_\sigma|z_H \pm \tfrac{1}{2}\rangle \end{aligned}\right\} \tag{6.32}$$

satisfying

$$\langle n_H \pm \tfrac{1}{2}|b_H \pm \tfrac{1}{2}\rangle = 0. \tag{6.33}$$

The coefficients t_σ and t_π are uniquely defined by demanding that the orbitals $|n_H \pm \tfrac{1}{2}\rangle$ not participating in the Kappa valence bond satisfy the orthogonality conditions

$$\langle n_H \pm \tfrac{1}{2}|v \pm \tfrac{1}{2}\rangle = 0. \tag{6.34}$$

The condition (6.34) ensures that the wavefunction

$$\begin{aligned} |\psi_{\kappa vb}\rangle = S_b \hat{\mathscr{A}}[|\mathrm{core}\rangle|\mathrm{core}_H\rangle|p_H \tfrac{3}{2}\rangle|p_H -\tfrac{3}{2}\rangle|n_H \tfrac{1}{2}\rangle|n_H -\tfrac{1}{2}\rangle \tfrac{1}{\sqrt{2}}(|v\tfrac{1}{2}\rangle|b_H -\tfrac{1}{2}\rangle \\ \pm|v-\tfrac{1}{2}\rangle|b_H \tfrac{1}{2}\rangle)], \end{aligned} \tag{6.35}$$

which describes the formation of a Kappa valence bond between the halogen bonding orbitals $|b_H \pm \tfrac{1}{2}\rangle$ and the orbitals $|v \pm \tfrac{1}{2}\rangle$, does not contain any destabilizing non-orthogonal Heitler–London triplet interactions arising from the overlap of the orbitals forming the bond with those not participating in the bond.

The total energy ($E_{T\kappa vb}$) calculated as the expectation value of the Brown hamiltonian is found, by making the usual assumptions of core orthogonality and invoking (6.19), to be

$$\begin{aligned} E_{T\kappa vb} = {} & E_{CE} + E_{CH} + 2(\langle p_H \tfrac{3}{2}|\hat{\mathscr{H}}_D + \hat{V}_{DFE} + \hat{V}_{CHDF} + \hat{G}_4|p_H \tfrac{3}{2}\rangle \\ & + \langle n_H \tfrac{1}{2}|\hat{\mathscr{H}}_D + \hat{V}_{DFE} + \hat{V}_{CHDF} + \tfrac{1}{2}\hat{G}_{nH-\frac{1}{2},\, nH-\frac{1}{2}}|n_H \tfrac{1}{2}\rangle + 2R^{-1}) \\ & + S_b^2(\langle b_H \tfrac{1}{2}|\hat{h}_b|b_H \tfrac{1}{2}\rangle + \langle v\tfrac{1}{2}|\hat{h}_b|v\tfrac{1}{2}\rangle \mp 2\langle b_H -\tfrac{1}{2}|v -\tfrac{1}{2}\rangle\langle v\tfrac{1}{2}|\hat{h}_b|b_H \tfrac{1}{2}\rangle \\ & + \langle v\tfrac{1}{2} b_H -\tfrac{1}{2}|r_{12}^{-1}|v\tfrac{1}{2} b_H -\tfrac{1}{2}\rangle \pm \langle v\tfrac{1}{2} b_H -\tfrac{1}{2}|r_{12}^{-1}|v -\tfrac{1}{2} b_H \tfrac{1}{2}\rangle \\ & \mp \langle v\tfrac{1}{2} b_H -\tfrac{1}{2}|r_{12}^{-1}|b_H \tfrac{1}{2} v -\tfrac{1}{2}\rangle - \langle v\tfrac{1}{2} b_H -\tfrac{1}{2}|r_{12}^{-1}|b_H -\tfrac{1}{2} v\tfrac{1}{2}\rangle) + R^{-1}, \end{aligned} \tag{6.36}$$

where

$$S_{\mathrm{b}} = (1+\langle \mathrm{v}\tfrac{1}{2}|\mathrm{b}_{\mathrm{H}}\tfrac{1}{2}\rangle^{2})^{-\frac{1}{2}}, \tag{6.37a}$$

$$\hat{\mathrm{G}}_{4} = \hat{\mathrm{G}}_{\mathrm{pH}\frac{3}{2},\,\mathrm{pH}\frac{3}{2}}+\hat{\mathrm{G}}_{\mathrm{pH}-\frac{3}{2},\,\mathrm{pH}-\frac{3}{2}}+\hat{\mathrm{G}}_{\mathrm{nH}\frac{1}{2},\,\mathrm{nH}\frac{1}{2}}+\hat{\mathrm{G}}_{\mathrm{nH}-\frac{1}{2},\,\mathrm{nH}-\frac{1}{2}}, \tag{6.37b}$$

$$\hat{\mathrm{h}}_{\mathrm{b}} = \hat{\mathscr{H}}_{\mathrm{D}}+\hat{V}_{\mathrm{DFE}}+\hat{V}_{\mathrm{CHDF}}+\hat{\mathrm{G}}_{4}. \tag{6.37c}$$

The interaction energy is extracted from (6.36) by invoking the Dirac–Fock equations (6.4) to show (cf. (6.16)) that

$$\begin{aligned}\langle \mathrm{v}\tfrac{1}{2}|\hat{\mathrm{h}}_{\mathrm{b}}|\mathrm{b}_{\mathrm{H}}\tfrac{1}{2}\rangle &= \langle \mathrm{v}\tfrac{1}{2}|\mathrm{b}_{\mathrm{H}}\tfrac{1}{2}\rangle\epsilon_{\mathrm{W}}+\langle \mathrm{v}\tfrac{1}{2}|\hat{\mathrm{G}}_{4}-\tfrac{4}{5}\hat{V}^{(0)}_{\mathrm{VH}}|\mathrm{b}_{\mathrm{H}}\tfrac{1}{2}\rangle \\ &= \langle \mathrm{v}\tfrac{1}{2}|\mathrm{b}_{\mathrm{H}}\tfrac{1}{2}\rangle\langle \mathrm{b}_{\mathrm{H}}\tfrac{1}{2}|\hat{\mathrm{h}}_{\mathrm{b}}|\mathrm{b}_{\mathrm{H}}\tfrac{1}{2}\rangle+\langle \mathrm{v}\tfrac{1}{2}|\hat{\mathrm{G}}_{4}-\tfrac{4}{5}\hat{V}^{(0)}_{\mathrm{VH}}|\mathrm{b}_{\mathrm{H}}\tfrac{1}{2}\rangle \\ &\quad -\langle \mathrm{v}\tfrac{1}{2}|\mathrm{b}_{\mathrm{H}}\tfrac{1}{2}\rangle\langle \mathrm{b}_{\mathrm{H}}\tfrac{1}{2}|\hat{\mathrm{G}}_{4}-\tfrac{4}{5}\hat{V}^{(0)}_{\mathrm{VH}}|\mathrm{b}_{\mathrm{H}}\tfrac{1}{2}\rangle\end{aligned} \tag{6.38}$$

and hence that

$$\begin{aligned}E_{\mathrm{int}}(\kappa\mathrm{vb}) &= 2(\langle \mathrm{p}_{\mathrm{H}}\tfrac{3}{2}|\hat{V}_{\mathrm{TE}}|\mathrm{p}_{\mathrm{H}}\tfrac{3}{2}\rangle+\langle \mathrm{n}_{\mathrm{H}}\tfrac{1}{2}|\hat{V}_{\mathrm{TE}}|\mathrm{n}_{\mathrm{H}}\tfrac{1}{2}\rangle+2R^{-1})+S_{\mathrm{b}}^{2}(\langle \mathrm{b}_{\mathrm{H}}\tfrac{1}{2}|\hat{V}_{\mathrm{TE}}|\mathrm{b}_{\mathrm{H}}\tfrac{1}{2}\rangle \\ &\quad +\langle \mathrm{v}\tfrac{1}{2}|\hat{V}_{\mathrm{NH}}+\hat{V}_{\mathrm{CHDF}}+\hat{\mathrm{G}}_{4}|\mathrm{v}\tfrac{1}{2}\rangle\mp 2\langle \mathrm{b}_{\mathrm{H}}-\tfrac{1}{2}|\mathrm{v}-\tfrac{1}{2}\rangle\langle \mathrm{v}\tfrac{1}{2}|\hat{V}_{\mathrm{NH}}+\hat{V}_{\mathrm{CHDF}}+\hat{\mathrm{G}}_{4}+\hat{V}_{\mathrm{TE}}|\mathrm{b}_{\mathrm{H}}\tfrac{1}{2}\rangle \\ &\quad +\langle \mathrm{v}\tfrac{1}{2}\mathrm{b}_{\mathrm{H}}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{v}\tfrac{1}{2}\mathrm{b}_{\mathrm{H}}-\tfrac{1}{2}\rangle\pm\langle \mathrm{v}\tfrac{1}{2}\mathrm{b}_{\mathrm{H}}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{v}-\tfrac{1}{2}\mathrm{b}_{\mathrm{H}}\tfrac{1}{2}\rangle \\ &\quad \mp\langle \mathrm{v}\tfrac{1}{2}\mathrm{b}_{\mathrm{H}}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{b}_{\mathrm{H}}\tfrac{1}{2}\mathrm{v}-\tfrac{1}{2}\rangle-\langle \mathrm{v}\tfrac{1}{2}\mathrm{b}_{\mathrm{H}}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{b}_{\mathrm{H}}-\tfrac{1}{2}\mathrm{v}\tfrac{1}{2}\rangle)+R^{-1}\mp R_{4}\end{aligned} \tag{6.39}$$

with

$$R_{4} = \langle \mathrm{b}_{\mathrm{H}}-\tfrac{1}{2}|\mathrm{v}-\tfrac{1}{2}\rangle(\langle \mathrm{v}\tfrac{1}{2}|\hat{\mathrm{G}}_{4}-\tfrac{4}{5}\hat{V}^{(0)}_{\mathrm{VH}}|\mathrm{b}_{\mathrm{H}}\tfrac{1}{2}\rangle-\langle \mathrm{v}\tfrac{1}{2}|\mathrm{b}_{\mathrm{H}}\tfrac{1}{2}\rangle\langle \mathrm{b}_{\mathrm{H}}\tfrac{1}{2}|\hat{\mathrm{G}}_{4}-\tfrac{4}{5}\hat{V}^{(0)}_{\mathrm{VH}}|\mathrm{b}_{\mathrm{H}}\tfrac{1}{2}\rangle). \tag{6.40}$$

In Appendix 6 it is shown that R_4 makes a negligible contribution to E_{int}. Before substituting the large components (3.9) into (6.39) and expressing the result in terms of (6.26), it is useful to note the identities

$$\left.\begin{aligned}\langle \mathrm{p}_{1,\mu}\mathrm{p}_{-1,\mu'}|r_{12}^{-1}|\mathrm{p}_{1,\mu}\mathrm{p}_{-1,\mu'}\rangle &= \langle \mathrm{p}_{1,\mu}\mathrm{p}_{1,\mu'}|r_{12}^{-1}|\mathrm{p}_{1,\mu}\mathrm{p}_{1,\mu'}\rangle, \\ \langle \mathrm{p}_{1,\mu}\mathrm{p}_{-1,\mu'}|r_{12}^{-1}|\mathrm{p}_{1,\mu'}\mathrm{p}_{-1,\mu}\rangle &= \langle \mathrm{p}_{1,\mu}\mathrm{p}_{1,\mu'}|r_{12}^{-1}|\mathrm{p}_{1,\mu'}\mathrm{p}_{1,\mu}\rangle.\end{aligned}\right\} \tag{6.41}$$

These are derived by using the standard expansion of r_{12}^{-1}

$$r_{12}^{-1} = 4\pi\sum_{k}(2k+1)^{-1}(r_{<}^{k}/r_{>}^{k+1})\sum_{m}\mathrm{Y}_{k,m}(\theta_1,\phi_1)\,\mathrm{Y}_{k,-m}(\theta_2,\phi_2)\,(-1)^{m},$$

writing $\mathrm{p}_{1,\mu}$ as $\mathrm{F}(r_\mu)\mathrm{Y}_{l,m}(\theta_\mu,\phi_\mu)$ and then noting that the integrals on the left and right hand sides of (6.41) become identical after integration over ϕ_1 and ϕ_2. Expressing (6.39) in terms of the large components and invoking (6.41) yields the interaction energy

$$\begin{aligned}E_{\mathrm{int}}(\kappa\mathrm{vb}) &= 2(\langle \mathrm{p}_{1,\mathrm{H}}|\hat{V}_{\mathrm{E}}|\mathrm{p}_{1,\mathrm{H}}\rangle+\langle \mathrm{n}_{\mathrm{H}}\tfrac{1}{2}|\hat{V}_{\mathrm{E}}|\mathrm{n}_{\mathrm{H}}\tfrac{1}{2}\rangle_{\mathrm{L}}+2R^{-1}) \\ &\quad +\{1+[t_{\pi}\sqrt{a}\langle \mathrm{p}_{0}|\mathrm{p}_{0,\mathrm{H}}\rangle\pm t_{\sigma}(1-a)^{\frac{1}{2}}\langle \mathrm{p}_{1,\mathrm{H}}|\mathrm{p}_{1}\rangle]^{2}\}^{-1} \\ &\quad \times\{t_{\pi}a\,{}^{1,\mathrm{N}}H_{\mathrm{int}}(\mathrm{p}_{0},\mathrm{p}_{0,\mathrm{H}},V_{\mathrm{E}},V_{\mathrm{H,b}})+t_{\sigma}^{2}(1-a)\,{}^{1,\mathrm{N}}H_{\mathrm{int}}(\mathrm{p}_{1},\mathrm{p}_{1,\mathrm{H}},V_{\mathrm{E}},V_{\mathrm{H,b}}) \\ &\quad \pm\tfrac{\sqrt{2}}{3}t_{\sigma}t_{\pi}X_{\mathrm{int}}(\mathrm{p}_{0},\mathrm{p}_{0,\mathrm{H}},\mathrm{p}_{1},\mathrm{p}_{1,\mathrm{H}},V_{\mathrm{E}},V_{\mathrm{H,b}})+t_{\pi}^{2}(1-a)\,{}^{3,0}H_{\mathrm{int}}(\mathrm{p}_{1},\mathrm{p}_{0,\mathrm{H}},V_{\mathrm{E}},V_{\mathrm{H,b}}) \\ &\quad +t_{\sigma}^{2}a\,{}^{3,0}H_{\mathrm{int}}(\mathrm{p}_{0},\mathrm{p}_{1,\mathrm{H}},V_{\mathrm{E}},V_{\mathrm{H,b}})\mp\tfrac{\sqrt{2}}{3}t_{\sigma}t_{\pi}(\langle \mathrm{p}_{0}\mathrm{p}_{0,\mathrm{H}}|r_{12}^{-1}|\mathrm{p}_{-1,\mathrm{H}}\mathrm{p}_{1}\rangle \\ &\quad +\langle \mathrm{p}_{1}\mathrm{p}_{-1,\mathrm{H}}|r_{12}^{-1}|\mathrm{p}_{0,\mathrm{H}}\mathrm{p}_{0}\rangle)\},\end{aligned} \tag{6.42}$$

where

$$\begin{aligned}X_{\mathrm{int}}(d,e,\mathrm{f},\mathrm{g},V_{\mu},V_{\mu'}) &= \langle d|e\rangle\langle \mathrm{f}|\hat{V}_{\mu}+\hat{V}_{\mu'}+R^{-1}|\mathrm{g}\rangle \\ &\qquad +\langle \mathrm{f}|\mathrm{g}\rangle\langle d|\hat{V}_{\mu}+\hat{V}_{\mu'}+R^{-1}|e\rangle+2\langle d\mathrm{f}|r_{12}^{-1}|e\mathrm{g}\rangle,\end{aligned} \tag{6.43}$$

$$\hat{V}_{\mathrm{H,b}} = \hat{V}_{\mathrm{NH}}+\hat{V}'_{\mathrm{CHDF}}+2(\hat{\mathrm{J}}_{\mathrm{p}_{1},\mathrm{H}}+\hat{\mathrm{J}}_{\mathrm{nH,L}})-\hat{\mathrm{K}}_{\mathrm{p}_{1},\mathrm{H}}-\hat{\mathrm{K}}_{\mathrm{nH,L}}. \tag{6.44}$$

The quantity $\hat{\mathrm{J}}_{\mathrm{nH,L}}$ is a coulomb operator built from the large components of the orbital $|\mathrm{n}_{\mathrm{H}}\tfrac{1}{2}\rangle$, while $\hat{\mathrm{K}}_{\mathrm{nH,L}}$ is derived from the spatial parts of the large components of this orbital.

Thus the matrix elements of these operators between the spinless one-component functions $|d\rangle$ and $|e\rangle$ are defined by

$$\left.\begin{aligned}\langle d|\hat{\mathrm{J}}_{\mathrm{nH,L}}|e\rangle &= t_\pi^2\langle d\mathrm{p}_{1,\mathrm{H}}|r_{12}^{-1}|e\mathrm{p}_{1,\mathrm{H}}\rangle + t_\sigma^2\langle d\mathrm{p}_{0,\mathrm{H}}|r_{12}^{-1}|e\mathrm{p}_{0,\mathrm{H}}\rangle,\\ \langle d|\hat{\mathrm{K}}_{\mathrm{nH,L}}|e\rangle &= t_\pi^2\langle d\mathrm{p}_{1,\mathrm{H}}|r_{12}^{-1}|\mathrm{p}_{1,\mathrm{H}}e\rangle + t_\sigma^2\langle d\mathrm{p}_{0,\mathrm{H}}|r_{12}^{-1}|\mathrm{p}_{0,\mathrm{H}}e\rangle.\end{aligned}\right\} \tag{6.45}$$

The notation $\langle \mathrm{n_H}\,\tfrac{1}{2}|\hat{V}_{\mathrm{E}}|\mathrm{n_H}\,\tfrac{1}{2}\rangle_{\mathrm{L}}$ in (6.42) denotes that the large components of the matrix element are taken.

The terms in the first brackets in the interaction energy (6.42), which arise from the halogen orbitals not directly participating in the Kappa valence bond, resemble part of the coulomb contribution to the interaction energy predicted by a Heitler–London wavefunction. Although these terms are probably quantitatively non-negligible, they will be sufficiently small that they do not determine the qualitative features of the bonding. Hence they will not be considered further. The condition (6.34) becomes

$$\mp t_\sigma a^{\frac{1}{2}}\langle \mathrm{p}_{0,\mathrm{H}}|\mathrm{p}_0\rangle + t_\pi(1-a)^{\frac{1}{2}}\langle \mathrm{p}_{1,\mathrm{H}}|\mathrm{p}_1\rangle = 0, \tag{6.46}$$

if only the large components are retained. This relation shows that, with the coordinate system of figure 1 for which the overlap $\langle \mathrm{p}_0|\mathrm{p}_{0,\mathrm{H}}\rangle$ is negative for the internuclear separations corresponding to bond formation, the quantities t_σ and t_π have opposite signs if $|\mathrm{v}\rangle$ is a $\bar{\mathrm{p}}$ orbital but the same sign if it is a p one. Since the quantity $X_{\mathrm{int}}(d, e, \mathrm{f}, \mathrm{g}, V_\mu, V_{\mu'})$ resembles two of the exchange contributions to the interaction energy of a non-orthogonal Heitler–London wavefunction, it follows that all the terms in (6.42) are negative except for the two exchange integrals. These two integrals can be neglected because they will be small and moreover their contribution to the interaction energy is opposite in sign to the already neglected contribution of the non-bonding valence electrons on the halogen. Hence the result (6.42) shows that the bonding described by the wavefunction (6.35) consists of both non-orthogonal Heitler–London singlet and orthogonal triplet contributions, which are augmented by two further non-orthogonal Heitler–London singlet exchange terms ($X_{\mathrm{int}}(\mathrm{p}_0, \mathrm{p}_{0,\mathrm{H}}, \mathrm{p}_1, \mathrm{p}_{1,\mathrm{H}}, V_{\mathrm{E}}, \hat{V}_{\mathrm{H,b}})$). The orders of the $\bar{\mathrm{p}}$–Hal and p–Hal bonds are thus predicted in the limit of small overlaps to be $\frac{2}{3}+\frac{1}{6}t_\sigma^2-\frac{2\sqrt{2}}{3}t_\sigma t_\pi$ and $\frac{2}{3}+\frac{1}{6}t_\pi^2+\frac{2\sqrt{2}}{3}t_\sigma t_\pi$ respectively if the orders of non-orthogonal singlet and orthogonal triplet bonds are taken to be 1 and $\frac{1}{2}$ respectively and a single term $X_{\mathrm{int}}(d, e, \mathrm{f}, \mathrm{g}, V_\mu, V_{\mu'})$ is taken to contribute -2 to the bond order. Although the latter may be a crude approximation because it neglects the coulomb contribution to the energy of a covalent bond which can be far from negligible (Fraga & Mulliken 1960), it is sufficient to reveal the qualitative features of the bonding. If the two overlaps $\langle \mathrm{p}_0|\mathrm{p}_{0,\mathrm{H}}\rangle$ and $\langle \mathrm{p}_1|\mathrm{p}_{1,\mathrm{H}}\rangle$ are equal in magnitude, the orders of the $\bar{\mathrm{p}}$–Hal and p–Hal bonds, (6.35), are both predicted to be $\frac{11}{9}$. It is interesting to observe that both $\bar{\mathrm{p}}$–Hal and p–Hal bonds are predicted to have bond orders of unity if the orthogonal triplet contributions are disregarded entirely. If both the coulomb contribution and the exchange integral in (6.28) were so small that the orthogonal triplet contribution was negligible, then the approximation that a single term X_{int} contributes -2 to the bond order would become quite accurate. It has been shown, regardless of the orthogonal triplet contribution to the bond order, that purely covalent bonds between a halogen and a heavy element containing a single $\bar{\mathrm{p}}$ or p valence electron are not destabilized by relativity. The meaning of a prediction of a bond order greater than unity is examined in §8.

The above calculation of the bond orders does not consider any possible difference between the strength of a non-orthogonal Heitler–London singlet bond constructed from σ orbitals and one constructed from π orbitals. A σ bond might be expected to be stronger than a π bond at large internuclear distances although there is no reason for supposing that this is a major factor at the equilibrium separation. However, the success of simple valence theory, which neglects any such distinction, in explaining the bonding in the first-row diatomics suggests that no essential features of p̄–Hal and p–Hal bonds are missed by neglecting this difference. The details of an investigation of the relative strengths of σ and π bonds, which would depend on the equilibrium internuclear separation and the nature of the outermost core orbitals, lie outside the scope of this study. Finally, it should be pointed out that the qualitative features of the bonding deduced in this subsection, in particular the condition (6.34) determining the orbitals, are essentially unaffected by any possible s–p hybridization of the halogen.

(iii) *Alternative modes of* p–Hal *bonding*

The wavefunction (6.35) does not describe the only possible mode of covalent bonding between a halogen and an element containing a single valence p electron because the valence orbitals having $m_j = \pm\frac{3}{2}$ are also available for bonding. Thus a calculation essentially identical to that used to derive (6.42) from (6.35) shows that the interaction energy predicted by the wavefunction

$$|\psi_{\kappa v\pi}\rangle = S_\pi \hat{\mathscr{A}}[|\mathrm{core}\rangle|\mathrm{core_H}\rangle|z_\mathrm{H}\,\tfrac{1}{2}\rangle|z_\mathrm{H}\,-\tfrac{1}{2}\rangle|\pi_{1,\mathrm{H}}\,\tfrac{1}{2}\rangle|\pi_{-1,\mathrm{H}}\,-\tfrac{1}{2}\rangle \\ \times\tfrac{1}{\sqrt{2}}(|\mathrm{p}\tfrac{3}{2}\rangle|\mathrm{p_H}\,-\tfrac{3}{2}\rangle-|\mathrm{p}\,-\tfrac{3}{2}\rangle|\mathrm{p_H}\,\tfrac{3}{2}\rangle)] \qquad (6.47)$$

is given by

$$E_\mathrm{int}(\kappa v\pi) = 2(\langle \mathrm{p_{0,H}}|\hat{V}_\mathrm{E}|\mathrm{p_{0,H}}\rangle+\langle \mathrm{p_{1,H}}|\hat{V}_\mathrm{E}|\mathrm{p_{1,H}}\rangle+2R^{-1}) \\ +(1+\langle \mathrm{p_1}|\mathrm{p_{1,H}}\rangle^2)^{-1\,1,\mathrm{N}}H_\mathrm{int}(\mathrm{p_1},\mathrm{p_{1,H}},V_\mathrm{E},V_{\mathrm{H},\pi})+R_5, \qquad (6.48)$$

where the halogen potential $\hat{V}_{\mathrm{H},\pi}$ is given by

$$\hat{V}_{\mathrm{H},\pi} = \hat{V}_\mathrm{NH}+\hat{V}'_\mathrm{CHDF}+2(\hat{\mathrm{J}}_{\mathrm{p_{1,H}}}+\hat{\mathrm{J}}_{\mathrm{p_{0,H}}})-\hat{\mathrm{K}}_{\mathrm{p_{0,H}}}-\hat{\mathrm{K}}_{\mathrm{p_{-1,H}}}. \qquad (6.49)$$

It is shown in Appendix 6 that the term R_5, which is both qualitatively similar to R_1, R_2 and R_4 and arises in the same way, is negligible. The result (6.48) shows that the wavefunction (6.47) describes the formation of a non-orthogonal Heitler–London singlet π bond of unit order.

It can be shown that there are non-vanishing off-diagonal matrix elements of the Brown hamiltonian between (6.47) and the function (6.35). However, the energy lowering occurring in the improved wavefunction constructed as a linear combination of these two functions should probably be interpreted as describing correlation of the bonding electrons rather than as a prediction of a bond order greater than unity.

The wavefunctions (6.35) and (6.47) taken in conjunction with the interaction energies (6.42) and (6.48) do show that the function

$$|\psi_{\kappa v2}\rangle = S_2 \hat{\mathscr{A}}[|\mathrm{core}\rangle|\mathrm{core_H}\rangle|\mathrm{n_H}\,\tfrac{1}{2}\rangle|\mathrm{n_H}\,-\tfrac{1}{2}\rangle\tfrac{1}{\sqrt{2}}(|\mathrm{p}\tfrac{3}{2}\rangle|\mathrm{p_H}\,-\tfrac{3}{2}\rangle-|\mathrm{p}\,-\tfrac{3}{2}\rangle|\mathrm{p_H}\,\tfrac{3}{2}\rangle) \\ \times\tfrac{1}{\sqrt{2}}(|\mathrm{p}\tfrac{1}{2}\rangle|\mathrm{b_H}\,-\tfrac{1}{2}\rangle-|\mathrm{p}\,-\tfrac{1}{2}\rangle|\mathrm{b_H}\,\tfrac{1}{2}\rangle)] \qquad (6.50)$$

is formally double bonded. However, since this function is ionic, corresponding to $\mathrm{E^-Hal^+}$, it cannot necessarily be concluded that a double bond is formed when a halogen interacts with a heavy element containing a single p valence electron. From the Kappa valence method one can predict only that such a bond will have an order greater than unity because the purely covalent functions (6.35) and (6.47) will become mixed with the double-bonded structure (6.50). The degree of mixing will depend upon the intrinsic strengths of the bonds compared with the sum of the electron affinity of the element E and the ionization potential of the halogen.

(iv) *The role of ionic–covalent resonance*

It has been shown that purely covalent single bonds between a halogen and an element containing a single unpaired electron in a $\bar{p}$ or a p orbital will not be weaker than a normal covalent σ bond. Any resonance stabilization of such bonds is likely to be dominated by interaction of the covalent function (6.35) with the ionic structure E^+Hal^- because any heavy element will be less electronegative than a halogen.

The wavefunction corresponding to the ionic structure E^+Hal^- can be written

$$|\psi_{\mathrm{H\,ion}}\rangle = \hat{\mathscr{A}}[|\mathrm{core}\rangle|\mathrm{core_H}\rangle|\mathrm{p_H}\tfrac{3}{2}\rangle|\mathrm{p_H}-\tfrac{3}{2}\rangle|\mathrm{n_H}\tfrac{1}{2}\rangle|\mathrm{n_H}-\tfrac{1}{2}\rangle|\mathrm{b_H}\tfrac{1}{2}\rangle|\mathrm{b_H}-\tfrac{1}{2}\rangle]. \qquad (6.51)$$

The resonance stabilization of the function $|\psi_{\kappa\mathrm{vb}}\rangle$ is investigated by introducing the hybrid $|\psi_{\mathrm{H\,res}}\rangle$ and the non-relativistic function $|\psi^{\mathrm{NR}}_{\mathrm{H\,res}}\rangle$, which is a resonance hybrid constructed from the covalent σ-bonded function $|{}^1\Sigma_{\mathrm{H}}\rangle$ and the ionic structure $|\psi^{\mathrm{NR}}_{\mathrm{H\,ion}}\rangle$:

$$|\psi_{\mathrm{H\,res}}\rangle = c_1|\psi_{\kappa\mathrm{vb}}\rangle + c_2|\psi_{\mathrm{H\,ion}}\rangle, \qquad (6.52a)$$

$$|\psi^{\mathrm{NR}}_{\mathrm{H\,res}}\rangle = c_1^{\mathrm{NR}}|{}^1\Sigma_{\mathrm{H}}\rangle + c_2^{\mathrm{NR}}|\psi^{\mathrm{NR}}_{\mathrm{H\,ion}}\rangle, \qquad (6.52b)$$

where

$$|{}^1\Sigma_{\mathrm{H}}\rangle = (1+\langle \mathrm{p}_0^{\mathrm{NR}}|\mathrm{p}^{\mathrm{NR}}_{0,\mathrm{H}}\rangle^2)^{-\frac{1}{2}}\, \hat{\mathscr{A}}(|\mathrm{core}^{\mathrm{NR}}\rangle|\mathrm{core}^{\mathrm{NR}}_{\mathrm{H}}\rangle|\mathrm{p}^{\mathrm{NR}}_{1,\mathrm{H}}\,\alpha\rangle|\mathrm{p}^{\mathrm{NR}}_{-1,\mathrm{H}}\,\beta\rangle$$
$$\times|\mathrm{p}^{\mathrm{NR}}_{1,\mathrm{H}}\,\beta\rangle|\mathrm{p}^{\mathrm{NR}}_{-1,\mathrm{H}}\,\alpha\rangle|\mathrm{p}_0^{\mathrm{NR}}\mathrm{p}^{\mathrm{NR}}_{0,\mathrm{H}}\rangle\tfrac{1}{\sqrt{2}}|\alpha\beta-\beta\alpha\rangle), \qquad (6.53)$$

$$|\psi^{\mathrm{NR}}_{\mathrm{H\,ion}}\rangle = \hat{\mathscr{A}}(|\mathrm{core}^{\mathrm{NR}}\rangle|\mathrm{core}^{\mathrm{NR}}_{\mathrm{H}}\rangle|\mathrm{p}^{\mathrm{NR}}_{1,\mathrm{H}}\,\alpha\rangle|\mathrm{p}^{\mathrm{NR}}_{-1,\mathrm{H}}\,\beta\rangle|\mathrm{p}^{\mathrm{NR}}_{1,\mathrm{H}}\,\beta\rangle|\mathrm{p}^{\mathrm{NR}}_{1,\mathrm{H}}\,\alpha\rangle|\mathrm{p}^{\mathrm{NR}}_{0,\mathrm{H}}\,\alpha\rangle|\mathrm{p}^{\mathrm{NR}}_{0,\mathrm{H}}\,\beta\rangle). \qquad (6.54)$$

The details of the investigation are identical to those described (§3(*b*)) in the discussion of the resonance stabilization of hydrides except that the potential due to the proton, V_{H}, is replaced by those due to the nucleus plus both the core and the non-bonding halogen valence electrons. These potentials are for the functions (6.52*a*) and (6.52*b*) respectively

$$\hat{V}_{\mathrm{res}} = \hat{V}_{\mathrm{NH}} + \hat{V}_{\mathrm{CHDF}} + \hat{\mathrm{G}}_4, \qquad (6.55a)$$

$$\hat{V}^{\mathrm{NR}}_{\mathrm{res}} = \hat{V}_{\mathrm{NH}} + \hat{V}^{\mathrm{NR}}_{\mathrm{CHDF}} + \hat{V}_{z,\mathrm{H}} - \hat{\mathrm{K}}^{\mathrm{NR}}_{\mathrm{p_1,H}} - \hat{\mathrm{K}}^{\mathrm{NR}}_{\mathrm{p_{-1},H}}. \qquad (6.56b)$$

The qualitative difference between the resonance stabilizations of the two functions $|\psi_{\mathrm{res}}\rangle$, (3.13), and $|\psi^{\mathrm{NR}}_{\mathrm{res}}\rangle$, (3.14), was shown to arise from the difference between the two quantities $E_{\mathrm{int}}(i-\kappa\mathrm{v}) - \Delta E_{\mathrm{int}}(\kappa\mathrm{v})$ and $E_{\mathrm{int}}(i-{}^1\Sigma) - \Delta^{\mathrm{NR}}E_{\mathrm{int}}({}^1\Sigma)$, which are respectively the intermolecular contributions to the matrix elements

$$(\langle\psi_{\mathrm{ion}}| - \langle\psi_{\mathrm{ion}}|\psi_{\kappa\mathrm{v}}\rangle\langle\psi_{\kappa\mathrm{v}}|)\,(\mathscr{H}_{\mathrm{Br}} + Z_{\mathrm{E}}/R)\,|\psi_{\kappa\mathrm{v}}\rangle$$

and its non-relativistic analogue. The corresponding matrix elements responsible for the resonance stabilizations in the wavefunctions (6.52) are

$$(\langle\psi_{\mathrm{H\,ion}}| - \langle\psi_{\mathrm{H\,ion}}|\psi_{\kappa\mathrm{vb}}\rangle\langle\psi_{\kappa\mathrm{vb}}|)\,(\hat{\mathscr{H}}_{\mathrm{Br}} + Z_{\mathrm{E}}Z_{\mathrm{H}}/R)\,|\psi_{\kappa\mathrm{vb}}\rangle$$
$$= -\langle\psi_{\mathrm{H\,ion}}|\psi_{\kappa\mathrm{vb}}\rangle E_{\mathrm{int}}(\kappa\mathrm{vb}) + \sqrt{2}S_{\mathrm{b}}[\langle\mathrm{b_H}\tfrac{1}{2}|\mathrm{v}\tfrac{1}{2}\rangle(\langle\mathrm{b_H}\tfrac{1}{2}|\hat{V}_{\mathrm{TE}}|\mathrm{b_H}\tfrac{1}{2}\rangle + R^{-1})$$
$$+\langle\mathrm{b_H}\tfrac{1}{2}|\hat{V}_{\mathrm{res}}|\mathrm{v}\tfrac{1}{2}\rangle + \langle\mathrm{b_H}\tfrac{1}{2}\mathrm{b_H}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{v}\tfrac{1}{2}\mathrm{b_H}-\tfrac{1}{2}\rangle - \langle\mathrm{b_H}\tfrac{1}{2}\mathrm{b_H}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{b_H}-\tfrac{1}{2}\mathrm{v}\tfrac{1}{2}\rangle], \qquad (6.56a)$$

$$(\langle\psi^{\mathrm{NR}}_{\mathrm{H\,ion}}| - \langle\psi^{\mathrm{NR}}_{\mathrm{H\,ion}}|{}^1\Sigma_{\mathrm{H}}\rangle\langle{}^1\Sigma_{\mathrm{H}}|)\,(\hat{\mathscr{H}}^{\mathrm{NR}} + Z_{\mathrm{E}}Z_{\mathrm{H}}/R)\,|{}^1\Sigma_{\mathrm{H}}\rangle$$
$$= -\langle\psi^{\mathrm{NR}}_{\mathrm{H\,ion}}|{}^1\Sigma_{\mathrm{H}}\rangle E_{\mathrm{int}}({}^1\Sigma_{\mathrm{H}}) + (1+\langle\mathrm{p}_0^{\mathrm{NR}}|\mathrm{p}^{\mathrm{NR}}_{0,\mathrm{H}}\rangle^2)^{-\frac{1}{2}}\sqrt{2}[\langle\mathrm{p}^{\mathrm{NR}}_{0,\mathrm{H}}|\mathrm{p}_0^{\mathrm{NR}}\rangle(\langle\mathrm{p}^{\mathrm{NR}}_{0,\mathrm{H}}|\hat{V}_{\mathrm{TE}}|\mathrm{p}^{\mathrm{NR}}_{0,\mathrm{H}}\rangle + R^{-1})$$
$$+\langle\mathrm{p}^{\mathrm{NR}}_{0,\mathrm{H}}\,\alpha|\hat{V}_{\mathrm{res}}|\mathrm{p}_0^{\mathrm{NR}}\,\alpha\rangle + \langle\mathrm{p}^{\mathrm{NR}}_{0,\mathrm{H}}\mathrm{p}^{\mathrm{NR}}_{0,\mathrm{H}}|r_{12}^{-1}|\mathrm{p}_0^{\mathrm{NR}}\mathrm{p}^{\mathrm{NR}}_{0,\mathrm{H}}\rangle], \qquad (6.56b)$$

where $E_{\mathrm{int}}(^1\Sigma_{\mathrm{H}})$ is the interaction energy predicted by the wavefunction $|^1\Sigma_{\mathrm{H}}\rangle$, and $\hat{\mathscr{H}}^{\mathrm{NR}}$ is the non-relativistic many-electron hamiltonian excluding nuclear–nuclear repulsion. The two expressions (6.56) are very similar because substitution for $|\mathrm{b_H} \pm \tfrac{1}{2}\rangle$ from (6.32) shows that the term $\langle \mathrm{b_H}\tfrac{1}{2}\mathrm{b_H} - \tfrac{1}{2}|r_{12}^{-1}|\mathrm{b_H} - \tfrac{1}{2}\mathrm{v}\tfrac{1}{2}\rangle$ vanishes if only the large components are considered. Although it is not possible to make quite such a detailed comparison between $|\psi_{\mathrm{H\,res}}\rangle$ and $|\psi_{\mathrm{H\,res}}^{\mathrm{NR}}\rangle$ as was made between $|\psi_{\mathrm{res}}\rangle$ and $|\psi_{\mathrm{res}}^{\mathrm{NR}}\rangle$, any major qualitative differences between the wavefunctions (6.52) will be revealed by assuming that the overlaps $\langle \mathrm{p_{0,H}}|\mathrm{p_0}\rangle$ and $\langle \mathrm{p_{1,H}}|\mathrm{p_1}\rangle$ are equal in magnitude. Thus for when $|\mathrm{v}\rangle$ is a $\bar{\mathrm{p}}$ orbital, $t_\sigma = -\sqrt{\tfrac{2}{3}}$ and $t_\pi = \frac{1}{\sqrt{3}}$, while $t_\sigma = \frac{1}{\sqrt{3}}$ and $t_\pi = \sqrt{\tfrac{2}{3}}$ if $|\mathrm{v}\rangle$ is a p orbital. By using the same approach the matrix elements $\langle \mathrm{p_{0,H}}|\hat{V}'_{\mathrm{res}}|\mathrm{p_0}\rangle$ and $\langle \mathrm{p_{1,H}}|\hat{V}'_{\mathrm{res}}|\mathrm{p_1}\rangle$ will be approximately equal. It thus follows by expressing (6.56*a*) in terms of the large components that the matrix elements (6.56*a*) and (6.56*b*) will be approximately equal. This shows that the resonance stabilization of a p̄–Hal or a p–Hal bond (6.35) is no less than that of a bond between a halogen and a light element showing negligible relativistic effects.

(*b*) *The molecular orbital description of monohalides*

It is illuminating to examine the bonding between a halogen and the *j–j* coupled ground state of a heavy element containing a single p̄ or p valence electron by using relativistic molecular orbital theory. The results of this investigation both confirm the predictions of the Kappa valence method and yield further insights into the bonding.

A purely covalent bond between such an element and a halogen is described in relativistic molecular orbital theory by the wavefunction,

$$|\psi_{\mathrm{HMO}}\rangle = \hat{\mathscr{A}}(|\mathrm{core}\rangle|\mathrm{core_H}\rangle|\phi_1\tfrac{3}{2}\rangle|\phi_1-\tfrac{3}{2}\rangle|\phi_1\tfrac{1}{2}\rangle|\phi_1-\tfrac{1}{2}\rangle|\phi_2\tfrac{1}{2}\rangle|\phi_2-\tfrac{1}{2}\rangle), \tag{6.57}$$

where the valence molecular orbitals are expanded in the valence atomic orbitals of the halogen and the heavy element as discussed in §3(*c*i). The expansion coefficients c_{ti} and orbital energies are calculated by solving the matrix equations (3.29) with the molecular Fock operator $\hat{\mathrm{F}}_{\mathrm{M}}$ given by

$$\hat{\mathrm{F}}_{\mathrm{M}} = \hat{\mathscr{H}}_{\mathrm{k.e.}} + \hat{V}_{\mathrm{NE}} + \hat{V}_{\mathrm{DFE}} + \hat{V}_{\mathrm{NH}} + \hat{V}_{\mathrm{CHDF}} + \hat{V}_{\mathrm{val}}. \tag{6.58}$$

Here $\hat{V}_{\mathrm{val}}$ is the potential, constructed relativistic coulomb and exchange operators, due to the six valence electrons that occupy the orbitals $|\phi_i m\rangle$ in (6.57). For both p̄–Hal and p–Hal bonds, the molecular orbitals $|\phi_1\tfrac{1}{2}\rangle$ and $|\phi_2\tfrac{1}{2}\rangle$ are expanded in the three atomic orbitals $|\mathrm{v}\tfrac{1}{2}\rangle$, $|z_{\mathrm{H}}\tfrac{1}{2}\rangle$ and $|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle$, the usual assumption being made that the diagonal Fock matrix elements are equal, which is compatible with the idea of purely covalent bonding.

The essential qualitative features of the bonding arise as a consequence of both the assumption of equality of the diagonal Fock matrix elements and the smallness of the matrix element $\langle z_{\mathrm{H}}\tfrac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle$ compared with the other off-diagonal matrix elements of $\hat{\mathrm{F}}_{\mathrm{M}}$. The halogen Dirac–Fock equation (6.4) shows that $\langle z_{\mathrm{H}}\tfrac{1}{2}|\hat{\mathscr{H}}_{\mathrm{k.e.}} + \hat{V}_{\mathrm{NH}} + \hat{V}_{\mathrm{CHDF}} + \hat{V}_{\mathrm{VH}}^{(0)}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle = 0$ while the quantity $\langle z_{\mathrm{H}}\tfrac{1}{2}|\hat{V}_{\mathrm{NE}} + \Sigma_{\mathrm{c}}\hat{\mathrm{J}}_{\mathrm{c}}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle$ also vanishes if only the large components of the orbitals $|z_{\mathrm{H}}\tfrac{1}{2}\rangle$ and $|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle$ are retained. If $|r\rangle$ is an orbital whose large components have a sharp *z*-spin component (i.e. $|r\rangle_{\mathrm{L}} = |\mathrm{f}(r)\,\alpha\rangle$ or $|r\rangle_{\mathrm{L}} = |\mathrm{f}(r)\,\beta\rangle$), the quantity $\langle z_{\mathrm{H}}\tfrac{1}{2}|\hat{\mathrm{G}}_{r,r}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle$ vanishes if only the large components are considered. Although neither the orbitals $|\mathrm{c}\rangle$ nor the valence molecular orbitals $|\phi_i m\rangle$ in (6.57), which generate the potential $\hat{V}_{\mathrm{val}}$, have this property, it is shown in Appendix 7 that the only contributions to $\langle z_{\mathrm{H}}\tfrac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle$ not so far considered, namely $\langle z_{\mathrm{H}}\tfrac{1}{2}|\hat{V}_{\mathrm{val}}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle$ and $-\langle z_{\mathrm{H}}\tfrac{1}{2}|\Sigma_{\mathrm{c}}\hat{\mathrm{K}}_{\mathrm{c}}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle$, are sufficiently small that they can be neglected.

Hence the matrix element $\langle z_{\mathrm{H}}\frac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|\pi_{1,\mathrm{H}}\frac{1}{2}\rangle$ can be taken to vanish. Denoting the three atomic orbitals $|\mathrm{v}\frac{1}{2}\rangle$, $|\pi_{1,\mathrm{H}}\frac{1}{2}\rangle$ and $|z_{\mathrm{H}}\frac{1}{2}\rangle$ by 1, 2 and 3, solution of the 3×3 secular problem (3.29) for the orbitals having $m_j = \frac{1}{2}$ yields a molecular orbital, denoted $|\phi_2\frac{1}{2}\rangle$, of energy $\langle z_{\mathrm{H}}\frac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|z_{\mathrm{H}}\frac{1}{2}\rangle$, which does not contain the orbital $|\mathrm{v}\frac{1}{2}\rangle$ (i.e. $c_{21} = 0$). Simplifying the matrix elements $\langle z_{\mathrm{H}}\frac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{v}\frac{1}{2}\rangle$ and $\langle\pi_{1,\mathrm{H}}\frac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{v}\frac{1}{2}\rangle$ entering (3.29) and invoking the Dirac–Fock equation (6.37*a*) show that the coefficients c_{22} and c_{32} are determined by the normalization condition and

$$c_{22}(\langle\mathrm{v}\tfrac{1}{2}|\hat{V}_{\mathrm{pot}}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle-\langle\mathrm{v}\tfrac{1}{2}|\hat{V}_{\mathrm{pot}}|\mathrm{v}\tfrac{1}{2}\rangle\langle\mathrm{v}\tfrac{1}{2}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle)$$
$$+c_{32}(\langle\mathrm{v}\tfrac{1}{2}|\hat{V}_{\mathrm{pot}}|z_{\mathrm{H}}\tfrac{1}{2}\rangle-\langle\mathrm{v}\tfrac{1}{2}|\hat{V}_{\mathrm{pot}}|\mathrm{v}\tfrac{1}{2}\rangle\langle\mathrm{v}\tfrac{1}{2}|z_{\mathrm{H}}\tfrac{1}{2}\rangle) = 0, \quad (6.59)$$

with $\hat{V}_{\mathrm{pot}} = \hat{V}_{\mathrm{NH}}+\hat{V}_{\mathrm{CHDF}}+\hat{V}_{\mathrm{val}}$. The equality of the energy ϵ_2 of the orbital $|\phi_2\frac{1}{2}\rangle$ to the diagonal Fock matrix element $\langle z_{\mathrm{H}}\frac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|z_{\mathrm{H}}\frac{1}{2}\rangle$ taken in conjunction with its composition of only halogen orbitals shows that the orbitals $|\phi_2\frac{1}{2}\rangle$ and $|\phi_2-\frac{1}{2}\rangle$ are non-bonding orbitals containing a halogen lone pair. The two remaining orbitals having $m_j = \frac{1}{2}$, denoted $|\phi_1\frac{1}{2}\rangle$ and $|\phi_3\frac{1}{2}\rangle$, obtained by solving (3.29), have energies that are respectively more and less negative than $\langle z_{\mathrm{H}}\frac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|z_{\mathrm{H}}\frac{1}{2}\rangle$, thus suggesting that $|\phi_1\frac{1}{2}\rangle$ is a bonding and $|\phi_3\frac{1}{2}\rangle$ is an anti-bonding molecular orbital.

When $|\mathrm{v}\rangle$ is a $\bar{\mathrm{p}}$ orbital the molecular orbital $|\phi_1\frac{3}{2}\rangle$ is just $|\mathrm{p}_{\mathrm{H}}\frac{3}{2}\rangle$ so that it is predicted from (6.57) that four electrons occupy non-bonding orbitals located on the halogen leaving the remaining two valence electrons to occupy the bonding orbitals $|\phi_1\frac{1}{2}\rangle$ and $|\phi_1-\frac{1}{2}\rangle$. If $|\mathrm{v}\rangle$ is a p orbital the molecular orbital $|\phi_1\frac{3}{2}\rangle$, which is non-bonding in the $\bar{\mathrm{p}}$ case, is replaced by the fully bonding orbital $(\frac{1}{\sqrt{2}}S_\pi)(|\mathrm{p}\frac{3}{2}\rangle+|\mathrm{p}_{\mathrm{H}}\frac{3}{2}\rangle)$, where S_π is a normalization constant. Hence four electrons occupy bonding orbitals and two occupy non-bonding orbitals. The purely covalent bond between a halogen and the *j–j* coupled ground state of an element having three valence p electrons has either the configuration $\phi_1\frac{1}{2}$, $\phi_1-\frac{1}{2}$, $\phi_2\frac{1}{2}$, $\phi_2-\frac{1}{2}$, $\phi_1\frac{3}{2}$, $\phi_1-\frac{3}{2}$, $\phi_3\frac{1}{2}$, $\phi_3-\frac{1}{2}$ or the configuration $\phi_1\frac{1}{2}$, $\phi_1-\frac{1}{2}$, $\phi_2\frac{1}{2}$, $\phi_2-\frac{1}{2}$, $\phi_1\frac{3}{2}$, $\phi_1-\frac{3}{2}$, $\phi_2\frac{3}{2}$, $\phi_2-\frac{3}{2}$. In both descriptions four electrons occupy bonding orbitals and two occupy anti-bonding ones, while two are located entirely on the halogen. In the p case $|\phi_1\frac{3}{2}\rangle$ is a fully bonding orbital while $|\phi_2\frac{3}{2}\rangle = \frac{1}{\sqrt{2}}S'_\pi)$ $(|\mathrm{p}\frac{3}{2}\rangle-|\mathrm{p}_{\mathrm{H}}\frac{3}{2}\rangle)$ is fully anti-bonding so that if $|\phi_1\frac{1}{2}\rangle$ and $|\phi_3\frac{1}{2}\rangle$ are fully bonding and fully anti-bonding orbitals respectively, the orders of $\bar{\mathrm{p}}$–Hal and p–Hal bonds are predicted to be one and two while the p^3–Hal system is predicted to be singly bonded. For both $\bar{\mathrm{p}}$–Hal and p–Hal bonds the forms of the wavefunctions and predicted bond orders are very similar to those arising in the Kappa valence method.

The introduction of one further approximation shows that there is an even greater similarity between the predictions of the relativistic molecular orbital and Kappa valence methods. If the two matrix elements $\langle\mathrm{v}\frac{1}{2}|\hat{V}_{\mathrm{pot}}|\pi_{1,\mathrm{H}}\frac{1}{2}\rangle$ and $\langle\mathrm{v}\frac{1}{2}|\hat{V}_{\mathrm{pot}}|z_{\mathrm{H}}\frac{1}{2}\rangle$ are proportional to the overlap integrals $\langle\mathrm{v}\frac{1}{2}|\pi_{1,\mathrm{H}}\frac{1}{2}\rangle$ and $\langle\mathrm{v}\frac{1}{2}|z_{\mathrm{H}}\frac{1}{2}\rangle$, so that

$$\langle\mathrm{v}\tfrac{1}{2}|\hat{V}_{\mathrm{pot}}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle/\langle\mathrm{v}\tfrac{1}{2}|\hat{V}_{\mathrm{pot}}|z_{\mathrm{H}}\tfrac{1}{2}\rangle = \langle\mathrm{v}\tfrac{1}{2}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle/\langle\mathrm{v}\tfrac{1}{2}|z_{\mathrm{H}}\tfrac{1}{2}\rangle, \quad (6.60)$$

the condition (2.62) determining the non-bonding orbital becomes

$$c_{22}\langle\mathrm{v}\tfrac{1}{2}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle+c_{32}\langle\mathrm{v}\tfrac{1}{2}|z_{\mathrm{H}}\tfrac{1}{2}\rangle = 0. \quad (6.61)$$

This condition is identical to that, (6.34), determining the orbitals $|\mathrm{n}_{\mathrm{H}}\pm\frac{1}{2}\rangle$ in the Kappa valence method, so that both the relativistic molecular orbital and Kappa valence approaches predict the same halogen non-bonding orbitals. The Dirac–Fock equations (6.37*a*) show that the matrix elements $\langle \mathrm{v}\tfrac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle$ and $\langle \mathrm{v}\tfrac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|z_{\mathrm{H}}\tfrac{1}{2}\rangle$ are given by

$$\left.\begin{aligned}\langle \mathrm{v}\tfrac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle &= \epsilon_{\mathrm{v}}\langle \mathrm{v}\tfrac{1}{2}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle + \langle \mathrm{v}\tfrac{1}{2}|\hat{V}_{\mathrm{pot}}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle,\\ \langle \mathrm{v}\tfrac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|z_{\mathrm{H}}\tfrac{1}{2}\rangle &= \epsilon_{\mathrm{v}}\langle \mathrm{v}\tfrac{1}{2}|z_{\mathrm{H}}\tfrac{1}{2}\rangle + \langle \mathrm{v}\tfrac{1}{2}|\hat{V}_{\mathrm{pot}}|z_{\mathrm{H}}\tfrac{1}{2}\rangle.\end{aligned}\right\} \tag{6.62}$$

These results, taken in conjunction with the approximation (6.60), show that the bonding and anti-bonding molecular orbitals $|\phi_1\tfrac{1}{2}\rangle$ and $|\phi_3\tfrac{1}{2}\rangle$ are, with c_{32} defined to be positive,

$$\left.\begin{aligned}|\phi_1\tfrac{1}{2}\rangle &= \tfrac{1}{\sqrt{2}}S_1[|\mathrm{v}\tfrac{1}{2}\rangle + (c_{32}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle - c_{22}|z_{\mathrm{H}}\tfrac{1}{2}\rangle)],\\ |\phi_3\tfrac{1}{2}\rangle &= \tfrac{1}{\sqrt{2}}S_3[|\mathrm{v}\tfrac{1}{2}\rangle - (c_{32}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle - c_{22}|z_{\mathrm{H}}\tfrac{1}{2}\rangle)].\end{aligned}\right\} \tag{6.63}$$

If the magnitudes of the two overlaps $\langle \mathrm{p}_0|\mathrm{p}_{0,\mathrm{H}}\rangle$ and $\langle \mathrm{p}_1|\mathrm{p}_{1,\mathrm{H}}\rangle$ are taken to be equal, the large components of $|\phi_1\tfrac{1}{2}\rangle$ become

$$|\phi_1\tfrac{1}{2}\rangle_{\mathrm{L}} = S_1[\sqrt{a}\,\tfrac{1}{\sqrt{2}}|\mp(\mathrm{p}_0 - \mathrm{p}_{0,\mathrm{H}})\,\alpha\rangle + (1-a)^{\frac{1}{2}}\,\tfrac{1}{\sqrt{2}}|(\mathrm{p}_1 + \mathrm{p}_{1,\mathrm{H}})\,\beta\rangle]. \tag{6.64}$$

This shows that $|\phi_1\tfrac{1}{2}\rangle$ is a fully bonding orbital even though it is partially σ and partially π in character. This confirms the tentative conclusion of the last paragraph that the orders of $\bar{\mathrm{p}}$–Hal and p–Hal bonds are one and two respectively and that the p^3–Hal system is singly bonded. The charge distribution in the wavefunction (6.57) describing a p–Hal system is not uniform so that the assumption that the diagonal Fock matrix elements are equal may be quite poor. A fully self-consistent treatment might reduce the predicted bond order so that even for p–Hal bonds the relativistic molecular orbital and Kappa valence approaches agree in predicting that although the bond order is greater than one, it is probably not as large as two.

7. THE MOLECULAR ORBITAL DESCRIPTION OF p^2 DIHALIDES

(*a*) *The linear geometry*

Only relativistic molecular orbital theory will be used to investigate the bonding between two halogens and the *j–j* coupled ground state of a heavy element containing two valence electrons occupying Dirac–Fock p orbitals. The Kappa valence method is not considered because the molecular orbital results show that it is not possible to construct a localized description of the bonding of the type presented in §4(*b*ii) for dihydrides for either the linear or the bent geometries of the molecule. The only bent geometry considered in detail is that for which the Hal–E–Hal bond angle is 90°. The basic features of the bonding are revealed by considering only this and the linear geometry, while it is shown in Appendix 8 that other geometries differ only in yielding less simple forms for the molecular orbitals.

For the linear molecule, the molecular orbitals, denoted $|\phi_a m i_{\mathrm{p}} h_z\rangle$, are eigenfunctions of the operators $\hat{\mathrm{j}}_z$, $\hat{\mathrm{I}}_{\mathrm{t}}$ and $\hat{\mathrm{H}}_{z,\mathrm{t}}$. Both the valence orbitals of the heavy element E, $|\mathrm{p}\tfrac{3}{2}\rangle$ and $|\mathrm{p}-\tfrac{1}{2}\rangle$, are antisymmetric under $\hat{\mathrm{I}}_{\mathrm{t}}$ and are eigenfunctions of $\hat{\mathrm{H}}_{z,\mathrm{t}}'$ with eigenvalue *i*. The result (2.29) shows that out of the 16 valence orbitals only those eight having m_j quantum numbers of either $\tfrac{3}{2}$ or $-\tfrac{1}{2}$ need to be considered explicitly. The assumption that the system can be described as consisting of two halogens covalently bonded to the element E implies both that the diagonal Fock matrix elements in the atomic orbital basis are equal and that the interaction of orbitals on different halogens can be neglected. With these assumptions, after constructing symmetry-adapted combinations of halogen valence orbitals, the Fock matrix factorizes into 1 × 1 and 2 × 2 blocks except for the 3 × 3 block arising from the functions

$$|\mathrm{p}-\tfrac{1}{2}\rangle, (|z_{\mathrm{H},1}-\tfrac{1}{2}\rangle+|z_{\mathrm{H},2}-\tfrac{1}{2}\rangle)/\sqrt{2} \quad \text{and} \quad (|\pi_{-1,\mathrm{H},1}-\tfrac{1}{2}\rangle+|\pi_{-1,\mathrm{H},2}-\tfrac{1}{2}\rangle)/\sqrt{2}.$$

The 1 × 1 and 2 × 2 blocks yield the molecular orbitals reported with their large components in Table 1. The 3 × 3 block has a form exactly analogous to that arising from $|\mathrm{v}\tfrac{1}{2}\rangle$, $|z_{\mathrm{H}}\tfrac{1}{2}\rangle$ and $|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle$ in the discussion (§6(*b*)) of monohalides. Since similar considerations show that $\frac{1}{\sqrt{2}}(\langle z_{\mathrm{H},1}-\tfrac{1}{2}|+\langle z_{\mathrm{H},2}-\tfrac{1}{2}|)\,\hat{\mathrm{F}}_{\mathrm{M}}\,\frac{1}{\sqrt{2}}(|\pi_{-1,\mathrm{H},1}-\tfrac{1}{2}\rangle+|\pi_{-1,\mathrm{H},2}-\tfrac{1}{2}\rangle)$ will be very small, it follows that one of the molecular orbitals obtained from the 3 × 3 block will be non-bonding and located entirely on the halogen. After evaluating the remaining off-diagonal Fock matrix elements by invoking the atomic Dirac–Fock equations (6.37*a*) and then using the approximation (6.60), one obtains two further molecular orbitals, one bonding and one anti-bonding. These three molecular orbitals are

$$\left.\begin{aligned}
|\phi_1-\tfrac{1}{2}-1i\rangle &= \tfrac{1}{\sqrt{2}}S_1\{|\mathrm{p}-\tfrac{1}{2}\rangle+[c_{32}\tfrac{1}{\sqrt{2}}(|\pi_{-1,\mathrm{H},1}-\tfrac{1}{2}\rangle+|\pi_{-1,\mathrm{H},2}-\tfrac{1}{2}\rangle)\\
&\qquad -c_{22}\tfrac{1}{\sqrt{2}}(|z_{\mathrm{H},1}-\tfrac{1}{2}\rangle+|z_{\mathrm{H},2}-\tfrac{1}{2}\rangle)]\},\\
|\phi_2-\tfrac{1}{2}-1i\rangle &= c_{22}\tfrac{1}{\sqrt{2}}(|\pi_{-1,\mathrm{H},1}-\tfrac{1}{2}\rangle+|\pi_{-1,\mathrm{H},2}-\tfrac{1}{2}\rangle)+c_{32}\tfrac{1}{\sqrt{2}}(|z_{\mathrm{H},1}-\tfrac{1}{2}\rangle+|z_{\mathrm{H},2}-\tfrac{1}{2}\rangle),\\
|\phi_3-\tfrac{1}{2}-1i\rangle &= \tfrac{1}{\sqrt{2}}S_3\{|\mathrm{p}-\tfrac{1}{2}\rangle-[(c_{32}\tfrac{1}{\sqrt{2}}(|\pi_{-1,\mathrm{H},1}-\tfrac{1}{2}\rangle+|\pi_{-1,\mathrm{H},2}-\tfrac{1}{2}\rangle)\\
&\qquad -c_{22}\tfrac{1}{\sqrt{2}}(|z_{\mathrm{H},1}-\tfrac{1}{2}\rangle+|z_{\mathrm{H},2}-\tfrac{1}{2}\rangle)]\},
\end{aligned}\right\}\qquad (7.1)$$

where the two positive coefficients c_{22} and c_{32} are determined by (6.61).

TABLE 1. MOLECULAR ORBITALS FOR LINEAR p^2 DIHALIDES IN THE LIMIT OF EQUAL OVERLAPS $|\langle \mathrm{p}_{0,\mathrm{H}}|\mathrm{p}_0\rangle|$ AND $\langle \mathrm{p}_{1,\mathrm{H}}|\mathrm{p}_1\rangle$

	relativistic molecular orbitals	energy relative to *d*†
$|\phi_1\tfrac{3}{2}-1i\rangle$	$S_1[\tfrac{1}{\sqrt{2}}|\mathrm{p}\tfrac{3}{2}\rangle+\tfrac{1}{2}(|\mathrm{p}_{\mathrm{H},1}\tfrac{3}{2}\rangle+|\mathrm{p}_{\mathrm{H},2}\tfrac{3}{2}\rangle)]$	$\sqrt{2}F$
$|\phi_2\tfrac{3}{2}-1i\rangle$	$S_2[\tfrac{1}{\sqrt{2}}|\mathrm{p}\tfrac{3}{2}\rangle-\tfrac{1}{2}(|\mathrm{p}_{\mathrm{H},1}\tfrac{3}{2}\rangle+|\mathrm{p}_{\mathrm{H},2}\tfrac{3}{2}\rangle)]$	$-\sqrt{2}F$
$|\phi_1-\tfrac{1}{2}-1i\rangle$	$S_1[\tfrac{1}{\sqrt{2}}|\mathrm{p}-\tfrac{1}{2}\rangle+\tfrac{1}{\sqrt{3}}\tfrac{1}{\sqrt{2}}(|\pi_{-1,\mathrm{H},1}-\tfrac{1}{2}\rangle+|\pi_{-1,\mathrm{H},2}-\tfrac{1}{2}\rangle)$ $-\sqrt{\tfrac{2}{3}}\tfrac{1}{\sqrt{2}}(|z_{\mathrm{H},1}-\tfrac{1}{2}\rangle+|z_{\mathrm{H},2}-\tfrac{1}{2}\rangle)]$	$\sqrt{2}F$
$|\phi_2-\tfrac{1}{2}-1i\rangle$	$\sqrt{\tfrac{2}{3}}\tfrac{1}{\sqrt{2}}(|\pi_{-1,\mathrm{H},1}-\tfrac{1}{2}\rangle+|\pi_{-1,\mathrm{H},2}-\tfrac{1}{2}\rangle)+\tfrac{1}{\sqrt{3}}\tfrac{1}{\sqrt{2}}(|z_{\mathrm{H},1}-\tfrac{1}{2}\rangle+|z_{\mathrm{H},2}-\tfrac{1}{2}\rangle)$	0
$|\phi_3-\tfrac{1}{2}-1i\rangle$	$S_2[\tfrac{1}{\sqrt{2}}|\mathrm{p}-\tfrac{1}{2}\rangle-\tfrac{1}{\sqrt{3}}\tfrac{1}{\sqrt{2}}(|\pi_{-1,\mathrm{H},1}-\tfrac{1}{2}\rangle+|\pi_{-1,\mathrm{H},2}-\tfrac{1}{2}\rangle)$ $+\sqrt{\tfrac{2}{3}}\tfrac{1}{\sqrt{2}}(|z_{\mathrm{H},1}-\tfrac{1}{2}\rangle+|z_{\mathrm{H},2}-\tfrac{1}{2}\rangle)]$	$-\sqrt{2}F$
$|\phi\tfrac{3}{2}1-i\rangle$	$\tfrac{1}{\sqrt{2}}(|\mathrm{p}_{\mathrm{H},1}\tfrac{3}{2}\rangle-|\mathrm{p}_{\mathrm{H},2}\tfrac{3}{2}\rangle)$	0
$|\phi_1-\tfrac{1}{2}1-i\rangle$	$\tfrac{1}{\sqrt{2}}(|z_{\mathrm{H},1}-\tfrac{1}{2}\rangle-|z_{\mathrm{H},2}-\tfrac{1}{2}\rangle)$	0
$|\phi_2-\tfrac{1}{2}1-i\rangle$	$\tfrac{1}{\sqrt{2}}(|\pi_{-1,\mathrm{H},1}-\tfrac{1}{2}\rangle-|\pi_{-1,\mathrm{H},2}-\tfrac{1}{2}\rangle)$	0
	large components	
$|\phi_1\tfrac{3}{2}-1i\rangle_{\mathrm{L}}$	$S_1[\tfrac{1}{\sqrt{2}}\mathrm{p}_1+\tfrac{1}{2}(\mathrm{p}_{1,\mathrm{H},1}+\mathrm{p}_{1,\mathrm{H},2})]|\alpha\rangle$	
$|\phi_2\tfrac{3}{2}-1i\rangle_{\mathrm{L}}$	$S_2[\tfrac{1}{\sqrt{2}}\mathrm{p}_1-\tfrac{1}{2}(\mathrm{p}_{1,\mathrm{H},1}+\mathrm{p}_{1,\mathrm{H},2})]|\alpha\rangle$	
$|\phi_1-\tfrac{1}{2}-1i\rangle_{\mathrm{L}}$	$S_1\{\sqrt{\tfrac{2}{3}}[\tfrac{1}{\sqrt{2}}\mathrm{p}_{0,\mathrm{H}}-\tfrac{1}{2}(\mathrm{p}_{0,\mathrm{H},1}+\mathrm{p}_{0,\mathrm{H},2})]|\beta\rangle+\tfrac{1}{\sqrt{3}}[\tfrac{1}{\sqrt{2}}\mathrm{p}_{-1}+\tfrac{1}{2}(\mathrm{p}_{-1,\mathrm{H},1}+\mathrm{p}_{-1,\mathrm{H},2})]|\alpha\rangle\}$	
$|\phi_2-\tfrac{1}{2}-1i\rangle_{\mathrm{L}}$	$\sqrt{\tfrac{2}{3}}\tfrac{1}{\sqrt{2}}(\mathrm{p}_{-1,\mathrm{H},1}+\mathrm{p}_{-1,\mathrm{H},2})|\alpha\rangle+\tfrac{1}{\sqrt{3}}\tfrac{1}{\sqrt{2}}(\mathrm{p}_{0,\mathrm{H},1}+\mathrm{p}_{0,\mathrm{H},2})|\beta\rangle$	
$|\phi_3-\tfrac{1}{2}-1i\rangle_{\mathrm{L}}$	$S_2\{\sqrt{\tfrac{2}{3}}[\tfrac{1}{\sqrt{2}}\mathrm{p}_{0,\mathrm{H}}+\tfrac{1}{2}(\mathrm{p}_{0,\mathrm{H},1}+\mathrm{p}_{0,\mathrm{H},2})]|\beta\rangle+\tfrac{1}{\sqrt{3}}[\tfrac{1}{\sqrt{2}}\mathrm{p}_{-1}-\tfrac{1}{2}(\mathrm{p}_{-1,\mathrm{H},1}+\mathrm{p}_{-1,\mathrm{H},2})]|\alpha\rangle\}$	
$|\phi\tfrac{3}{2}1-i\rangle_{\mathrm{L}}$	$\tfrac{1}{\sqrt{2}}(\mathrm{p}_{1,\mathrm{H},1}-\mathrm{p}_{1,\mathrm{H},2})|\alpha\rangle$	
$|\phi_1-\tfrac{1}{2}1-i\rangle_{\mathrm{L}}$	$\tfrac{1}{\sqrt{2}}(\mathrm{p}_{0,\mathrm{H},1}-\mathrm{p}_{0,\mathrm{H},2})|\beta\rangle$	
$|\phi_2-\tfrac{1}{2}1-i\rangle_{\mathrm{L}}$	$\tfrac{1}{\sqrt{2}}(\mathrm{p}_{-1,\mathrm{H},1}-\mathrm{p}_{-1,\mathrm{H},2})|\alpha\rangle$	

† In the limit of zero overlap *F* is defined by (7.7*b*).

For the case in which the overlaps $\langle \mathrm{p}_{0,\mathrm{H}}|\mathrm{p}_0\rangle$ and $\langle \mathrm{p}_{1,\mathrm{H}}|\mathrm{p}_1\rangle$ are equal in magnitude the molecular orbitals (7.1) are given in table 1. The large components of $|\phi_1 -\tfrac{1}{2} - 1i\rangle$ show that this molecular orbital is, like $|\phi_1 \tfrac{3}{2} - 1i\rangle$, a full three-centre bonding orbital. There are twelve valence electrons to accommodate in the 16 molecular orbitals consisting of the eight (table 1) having $m_j = \tfrac{3}{2}$ or $-\tfrac{1}{2}$ plus the further eight obtained by applying either of the operators $\hat{\mathrm{H}}_{x,\mathrm{t}}$ or $\hat{\mathrm{H}}_{y,\mathrm{t}}$ to those reported in table 1. Eight of these electrons occupy non-bonding orbitals located entirely on the halogens leaving four electrons to occupy three-centre bonding orbitals. This result which shows that two halogens are bound by four electrons strongly suggests that each halogen should be regarded as singly bonded to the heavy element.

(*b*) *The nonlinear geometry*

Since the molecular orbitals of the bent molecule cease to be eigenfunctions of either $\hat{\mathrm{j}}_z$ or $\hat{\mathrm{I}}_{\mathrm{t}}$, it follows that all eight symmetry-adapted combinations of atomic orbitals having eigenvalue i of $\hat{\mathrm{H}}_{z,\mathrm{t}}$ can interact. These eight combinations can be expressed in terms of the two orbitals $|\mathrm{p}\tfrac{3}{2}\rangle$ and $|\mathrm{p}-\tfrac{1}{2}\rangle$ and the six eigenfunctions of $\hat{\mathrm{H}}_{z,\mathrm{t}}$:

$$\left.\begin{aligned}
|\chi_{\mathrm{H},1}\rangle &= \tfrac{1}{\sqrt{2}}\left(|x_{\alpha,\mathrm{H},1}\rangle + |x_{\alpha,\mathrm{H},2}\rangle\right), & |\chi_{\mathrm{H},4}\rangle &= \tfrac{1}{\sqrt{2}}\left(|x_{\beta,\mathrm{H},1}\rangle - |x_{\beta,\mathrm{H},2}\rangle\right),\\
|\chi_{\mathrm{H},2}\rangle &= \tfrac{1}{\sqrt{2}}\left(|z_{\mathrm{H},1} - \tfrac{1}{2}\rangle + |z_{\mathrm{H},2} - \tfrac{1}{2}\rangle\right), & |\chi_{\mathrm{H},5}\rangle &= \tfrac{1}{\sqrt{2}}\left(|z_{\mathrm{H},2}\tfrac{1}{2}\rangle - |z_{\mathrm{H},1}\tfrac{1}{2}\rangle\right),\\
|\chi_{\mathrm{H},3}\rangle &= \tfrac{1}{\sqrt{2}}\left(|y_{\beta,\mathrm{H},1}\rangle - |y_{\beta,\mathrm{H},2}\rangle\right), & |\chi_{\mathrm{H},6}\rangle &= \tfrac{1}{\sqrt{2}}\left(|y_{\alpha,\mathrm{H},1}\rangle + |y_{\alpha,\mathrm{H},2}\rangle\right),
\end{aligned}\right\} \tag{7.2}$$

where

$$\left.\begin{aligned}
|x_{\alpha,\mathrm{H},\mu}\rangle &= \tfrac{1}{\sqrt{2}}\left(|\pi_{-1,\mathrm{H},\mu} - \tfrac{1}{2}\rangle - |\mathrm{p}_{\mathrm{H},\mu}\tfrac{3}{2}\rangle\right), & |x_{\beta,\mathrm{H},\mu}\rangle &= \tfrac{1}{\sqrt{2}}\left(|\mathrm{p}_{\mathrm{H},\mu} - \tfrac{3}{2}\rangle - |\pi_{1,\mathrm{H},\mu}\tfrac{1}{2}\rangle\right),\\
|y_{\alpha,\mathrm{H},\mu}\rangle &= \tfrac{1}{\sqrt{2}}\,i\left(|\pi_{-1,\mathrm{H},\mu} - \tfrac{1}{2}\rangle + |\mathrm{p}_{\mathrm{H},\mu}\tfrac{3}{2}\rangle\right), & |y_{\beta,\mathrm{H},\mu}\rangle &= \tfrac{1}{\sqrt{2}}\,\mathrm{i}\left(|\mathrm{p}_{\mathrm{H},\mu} - \tfrac{3}{2}\rangle + |\pi_{1,\mathrm{H},\mu}\tfrac{1}{2}\rangle\right).
\end{aligned}\right\} \tag{7.3}$$

Here the first suffix, α or β, denotes the *z*-spin associated with the large components while the further notation x or y shows that the spatial functions associated with the large components are p_x or p_y orbitals.

The orbitals $|\mathrm{p}m\rangle$ satisfy an atomic Dirac–Fock equation differing from (3.7*a*) only in the appearance of the additional potential $\hat{V}_{\mathrm{VE}}\ (= \tfrac{2}{3}\Sigma_{m=-\frac{3}{2}}^{\frac{3}{2}}(\hat{\mathrm{J}}_{\mathrm{v}m} - \hat{\mathrm{K}}_{\mathrm{v}m}))$. This Dirac–Fock equation shows that the matrix elements of the molecular Fock operator $\hat{\mathrm{F}}_{\mathrm{M}}$ can be expressed as

$$\langle \chi_{\mathrm{H},i}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}m\rangle = \epsilon_{\mathrm{v}}\langle \chi_{\mathrm{H},i}|\mathrm{p}m\rangle + \langle \chi_{\mathrm{H},i}|\hat{V}_{\mathrm{pot}}|\mathrm{p}m\rangle, \tag{7.4}$$

where $\hat{V}_{\mathrm{pot}}$ contains the potential $\hat{V}_{\mathrm{val}}$ due to the twelve valence electrons and that due to the two halogen cores:

$$\hat{V}_{\mathrm{pot}} = \hat{V}_{\mathrm{NH1}} + \hat{V}_{\mathrm{NH2}} + \hat{V}_{\mathrm{CH1DF}} + \hat{V}_{\mathrm{CH2DF}} + \hat{V}_{\mathrm{val}} - \hat{V}_{\mathrm{E}}. \tag{7.5}$$

It is useful to introduce the spatial p orbitals $\mathrm{p}_{\parallel,\mu}$ centred on atom μ (μ = E or halogen 1) and oriented along the E–Hal_1 bond, which can be expressed in terms of orbitals $\mathrm{p}_{x,\mu}$ and $\mathrm{p}_{z,\mu}$. The qualitative features of the bonding are revealed by assuming both that the quantities $\langle \chi_{\mathrm{H},i}|\hat{V}_{\mathrm{pot}}|\mathrm{p}m\rangle$ are proportional to the overlap integrals $\langle \chi_{\mathrm{H},i}|\mathrm{p}m\rangle$ and that the overlap between a pair of p orbitals directed along the bond is equal to that of a pair of p orbitals oriented perpendicular to the bond (i.e. $\langle \mathrm{p}_{\parallel}|\mathrm{p}_{\parallel,\mathrm{H}}\rangle = \langle \mathrm{p}_y|\mathrm{p}_{y,\mathrm{H}}\rangle$). Since the second assumption shows, for a bond angle of 90°, that

$$\left.\begin{aligned}
\langle \mathrm{p}_x|\mathrm{p}_{x,\mathrm{H},\mu}\rangle &= \langle \mathrm{p}_0|\mathrm{p}_{0,\mathrm{H},\mu}\rangle = 0, \quad \mu = 1, 2,\\
\langle \mathrm{p}_x|\mathrm{p}_{0,\mathrm{H},2}\rangle &= \langle \mathrm{p}_0|\mathrm{p}_{x,\mathrm{H},2}\rangle = -\langle \mathrm{p}_x|\mathrm{p}_{0,\mathrm{H},1}\rangle = -\langle \mathrm{p}_0|\mathrm{p}_{x,\mathrm{H},1}\rangle = \langle \mathrm{p}_y|\mathrm{p}_{y,\mathrm{H},1}\rangle,
\end{aligned}\right\} \tag{7.6}$$

it follows that all six Fock matrix elements $\langle \chi_{\mathrm{H},i}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}m\rangle$ ($i = 1, 2, 3$, $m = -\tfrac{1}{2}, \tfrac{3}{2}$) vanish if only the large components in (7.4) are retained. This shows that each of the three functions

$|\chi_{\mathrm{H},1}\rangle$, $|\chi_{\mathrm{H},2}\rangle$ and $|\chi_{\mathrm{H},3}\rangle$ is a non-bonding molecular orbital located entirely on the halogens. With these assumptions all the off-diagonal Fock matrix elements $\langle\chi_{\mathrm{H},i}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}m\rangle$ ($i = 4, 5, 6$, $m = -\frac{1}{2}, \frac{3}{2}$) are non-zero except $\langle\chi_{\mathrm{H},4}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}\frac{3}{2}\rangle$. These elements are calculated, by using (7.4) and (7.6), taking $\langle\chi_{\mathrm{H},i}|\hat{V}_{\mathrm{pot}}|\mathrm{p}m\rangle$ to be proportional to $\langle\chi_{\mathrm{H},i}|\mathrm{p}m\rangle$, and retaining only the large components, to be

$$\left.\begin{aligned}\langle\chi_{\mathrm{H},4}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}\tfrac{3}{2}\rangle &= 0, & \langle\chi_{\mathrm{H},4}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}-\tfrac{1}{2}\rangle &= -\tfrac{2}{\sqrt{3}}F,\\ \langle\chi_{\mathrm{H},5}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}\tfrac{3}{2}\rangle &= -F, & \langle\chi_{\mathrm{H},5}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}-\tfrac{1}{2}\rangle &= \tfrac{1}{\sqrt{3}}F,\\ \langle\chi_{\mathrm{H},6}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}\tfrac{3}{2}\rangle &= -iF, & \langle\chi_{\mathrm{H},6}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}-\tfrac{1}{2}\rangle &= -\tfrac{1}{\sqrt{3}}iF.\end{aligned}\right\} \tag{7.7a}$$

Here the quantity F, defined as

$$F = \epsilon_{\mathrm{v}}\langle\mathrm{p}_{y,\mathrm{H},1}|\mathrm{p}_y\rangle + \langle\mathrm{p}_{y,\mathrm{H},1}|\hat{V}_{\mathrm{pot}}|\mathrm{p}_y\rangle \tag{7.7b}$$

with the matrix element of the potential $\hat{V}_{\mathrm{pot}}$ given in accordance with (3.10), is just the resonance integral for a non-relativistic bond orientated along the internuclear axis.

Although the functions entering (7.7) yield a 5×5 matrix, the forms deduced in §4(*b*ii) for the orbitals in dihydrides provide a key for calculating the molecular orbitals arising from these five functions without recourse either to the solution of a quintic equation or to computation. It is therefore useful to introduce the normalized hybrids $|\mathrm{v}_1 i\rangle$ and $|\mathrm{v}_2 i\rangle$ which appear in the dihydride molecular orbitals (4.31)

$$\left.\begin{aligned}|\mathrm{v}_1 i\rangle &= \tfrac{1}{2}(\sqrt{3}|\mathrm{p}-\tfrac{1}{2}\rangle - |\mathrm{p}\tfrac{3}{2}\rangle),\\ |\mathrm{v}_2 i\rangle &= \tfrac{1}{2}(|\mathrm{p}-\tfrac{1}{2}\rangle + \sqrt{3}|\mathrm{p}\tfrac{3}{2}\rangle),\end{aligned}\right\} \tag{7.8}$$

with large components

$$\left.\begin{aligned}|\mathrm{v}_1 i\rangle_{\mathrm{L}} &= \tfrac{1}{\sqrt{2}}(|\mathrm{p}_0\beta\rangle + |\mathrm{p}_x\alpha\rangle),\\ |\mathrm{v}_2 i\rangle_{\mathrm{L}} &= \tfrac{1}{\sqrt{6}}(|\mathrm{p}_0\beta\rangle - |\mathrm{p}_x\alpha\rangle) - i\sqrt{\tfrac{2}{3}}\,|\mathrm{p}_y\alpha\rangle.\end{aligned}\right\} \tag{7.9}$$

It follows, either by using (7.8) and the matrix elements (7.7) or by invoking the large components (7.9), that introduction of the two linear combinations

$$\left.\begin{aligned}|\chi'_{\mathrm{H},4}\rangle &= \tfrac{1}{\sqrt{2}}(|\chi_{\mathrm{H},5}\rangle - |\chi_{\mathrm{H},4}\rangle),\\ |\chi'_{\mathrm{H},5}\rangle &= \tfrac{1}{\sqrt{2}}(|\chi_{\mathrm{H},4}\rangle + |\chi_{\mathrm{H},5}\rangle)\end{aligned}\right\} \tag{7.10}$$

factorizes the 5×5 matrix into a 2×2 and a 3×3 matrix. Both the functions $|\mathrm{v}_1 i\rangle$ and $|\chi'_{\mathrm{H},4}\rangle$ have only one off-diagonal matrix element, namely $\langle\chi'_{\mathrm{H},4}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{v}_1 i\rangle = \sqrt{2}\,F$. These two functions therefore yield a bonding orbital $|\phi_1 i\rangle$ and an anti-bonding orbital $|\phi_7 i\rangle$ of energies $(\langle\mathrm{v}\tfrac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{v}\tfrac{1}{2}\rangle + \sqrt{2}\,F)\,S_{\mathrm{M}0}$ and $(\langle\mathrm{v}\tfrac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{v}\tfrac{1}{2}\rangle - \sqrt{2}\,F)\,S'_{\mathrm{M}0}$ where $S_{\mathrm{M}0}$ and $S'_{\mathrm{M}0}$ are normalization constants. The large components of the orbital $|\phi_1 i\rangle$ presented in table 2 confirm that this is a fully bonding orbital as suggested by its energy. The three remaining functions $|\mathrm{v}_2 i\rangle$, $|\chi'_{\mathrm{H},5}\rangle$ and $|\chi_{\mathrm{H},6}\rangle$ yield a 3×3 matrix $F_{\mathrm{M}3}$ whose elements calculated from (7.7), (7.8) and (7.10) are

$$F_{\mathrm{M}3} = \begin{bmatrix} d & -\sqrt{\tfrac{2}{3}}\,F & \tfrac{2}{\sqrt{3}}iF\\ -\sqrt{\tfrac{2}{3}}\,F & d & 0\\ -\tfrac{2}{\sqrt{3}}iF & 0 & d\end{bmatrix} \tag{7.11}$$

with d given in accordance with (7.7) by $\epsilon_{\mathrm{v}} + \langle\mathrm{p}_y|\hat{V}_{\mathrm{pot}}|\mathrm{p}_y\rangle$. Substitution of (7.11) into (3.29) yields one orbital ($|\phi_3 i\rangle$, table 2) of energy d containing no $|\mathrm{v}_2 i\rangle$ which is therefore a symmetry-adapted combination of non-bonding orbitals located entirely on the halogens. The two remaining molecular orbitals $|\phi_2 i\rangle$ and $|\phi_8 i\rangle$ obtained from (7.11) without neglecting overlap have energies $S_{\mathrm{M0}}(d+\sqrt{2}F)$ and $S_{\mathrm{M0}}\ (d-\sqrt{2}F)$. The large components presented in table 2 confirm the result suggested by its energy that $|\phi_2 i\rangle$ is a fully bonding orbital. The energy is the same as that of the non-relativistic three-centre bonding orbital $\frac{1}{2}(\mathrm{p}_{1,\mathrm{H},1}+\mathrm{p}_{1,\mathrm{H},2})+\frac{1}{\sqrt{2}}\mathrm{p}_1$.

TABLE 2. MOLECULAR ORBITALS FOR p^2 DIHALIDES WITH A Hal–E–Hal BOND ANGLE OF 90° WITH EQUAL OVERLAPS $|\langle \mathrm{p}_{0,\mathrm{H}}|\mathrm{p}_0\rangle|$ AND $\langle \mathrm{p}_{1,\mathrm{H}}|\mathrm{p}_1\rangle$

	relativistic molecular orbitals	energy relative to d†
$\lvert\phi_1 i\rangle$	$S_1[\frac{1}{2\sqrt{2}}(\sqrt{3}\lvert \mathrm{p}-\tfrac{1}{2}\rangle-\lvert \mathrm{p}\tfrac{3}{2}\rangle)+\frac{1}{2}(\lvert z_{\mathrm{H},2}\tfrac{1}{2}\rangle-\lvert z_{\mathrm{H},1}\tfrac{1}{2}\rangle)-\frac{1}{2}(\lvert x_{\beta,\mathrm{H},1}\rangle-\lvert x_{\beta,\mathrm{H},2}\rangle)]$	$\sqrt{2}\,F$
$\lvert\phi_2 i\rangle$	$S_1\{\frac{1}{2\sqrt{2}}(\lvert \mathrm{p}-\tfrac{1}{2}\rangle+\sqrt{3}\lvert \mathrm{p}\tfrac{3}{2}\rangle)-\frac{1}{\sqrt{12}}[\frac{1}{\sqrt{2}}(\lvert z_{\mathrm{H},2}\tfrac{1}{2}\rangle-\lvert z_{\mathrm{H},1}\tfrac{1}{2}\rangle)$ $+\frac{1}{\sqrt{2}}(\lvert x_{\beta,\mathrm{H},1}\rangle-\lvert x_{\beta,\mathrm{H},2}\rangle)]-\frac{1}{\sqrt{6}}i(\lvert y_{\alpha,\mathrm{H},1}\rangle+\lvert y_{\alpha,\mathrm{H},2}\rangle)\}$	$\sqrt{2}\,F$
$\lvert\phi_3 i\rangle$	$\frac{1}{\sqrt{6}}[\lvert z_{\mathrm{H},2}\tfrac{1}{2}\rangle-\lvert z_{\mathrm{H},1}\tfrac{1}{2}\rangle+\lvert x_{\beta,\mathrm{H},1}\rangle-\lvert x_{\beta,\mathrm{H},2}\rangle-i(\lvert y_{\alpha,\mathrm{H},1}\rangle+\lvert y_{\alpha,\mathrm{H},2}\rangle)]$	0
$\lvert\phi_4 i\rangle$	$\lvert\chi_{\mathrm{H},1}\rangle=\frac{1}{\sqrt{2}}(\lvert x_{\alpha,\mathrm{H},1}\rangle+\lvert x_{\alpha,\mathrm{H},2}\rangle)$	0
$\lvert\phi_5 i\rangle$	$\lvert\chi_{\mathrm{H},2}\rangle=\frac{1}{\sqrt{2}}(\lvert z_{\mathrm{H},1}-\tfrac{1}{2}\rangle+\lvert z_{\mathrm{H},2}-\tfrac{1}{2}\rangle)$	0
$\lvert\phi_6 i\rangle$	$\lvert\chi_{\mathrm{H},3}\rangle=\frac{1}{\sqrt{2}}(\lvert y_{\beta,\mathrm{H},1}\rangle-\lvert y_{\beta,\mathrm{H},2}\rangle)$	0
$\lvert\phi_7 i\rangle$	$S_2[\frac{1}{2\sqrt{2}}(\sqrt{3}\lvert \mathrm{p}-\tfrac{1}{2}\rangle-\lvert \mathrm{p}\tfrac{3}{2}\rangle)-\frac{1}{2}(\lvert z_{\mathrm{H},2}\tfrac{1}{2}\rangle-\lvert z_{\mathrm{H},1}\tfrac{1}{2}\rangle)+\frac{1}{2}(\lvert x_{\beta,\mathrm{H},1}\rangle-\lvert x_{\beta,\mathrm{H},2}\rangle)]$	$-\sqrt{2}\,F$
$\lvert\phi_8 i\rangle$	$S_2\{\frac{1}{2\sqrt{2}}(\lvert \mathrm{p}-\tfrac{1}{2}\rangle+\sqrt{3}\lvert \mathrm{p}\tfrac{3}{2}\rangle)+\frac{1}{\sqrt{12}}[\frac{1}{\sqrt{2}}(\lvert z_{\mathrm{H},2}\tfrac{1}{2}\rangle-\lvert z_{\mathrm{H},1}\tfrac{1}{2}\rangle)$ $+\frac{1}{\sqrt{2}}(\lvert x_{\beta,\mathrm{H},1}\rangle-\lvert x_{\beta,\mathrm{H},2}\rangle)]+\frac{1}{\sqrt{6}}i(\lvert y_{\alpha,\mathrm{H},1}\rangle+\lvert y_{\alpha,\mathrm{H},2}\rangle)\}$	$-\sqrt{2}\,F$
	large components	
$\lvert\phi_1 i\rangle_{\mathrm{L}}$	$S_1\frac{1}{\sqrt{2}}\{[\frac{1}{\sqrt{2}}\mathrm{p}_0-\frac{1}{2}(\mathrm{p}_{x,\mathrm{H},1}-\mathrm{p}_{x,\mathrm{H},2})]\lvert\beta\rangle+[\frac{1}{\sqrt{2}}\mathrm{p}_x+\frac{1}{2}(\mathrm{p}_{0,\mathrm{H},2}-\mathrm{p}_{0,\mathrm{H},1})]\lvert\alpha\rangle\}$	
$\lvert\phi_2 i\rangle_{\mathrm{L}}$	$S_1\{\frac{1}{\sqrt{6}}[\frac{1}{\sqrt{2}}\mathrm{p}_0-\frac{1}{2}(\mathrm{p}_{x,\mathrm{H},1}-\mathrm{p}_{x,\mathrm{H},2})]\lvert\beta\rangle-\frac{1}{\sqrt{6}}[\frac{1}{\sqrt{2}}\mathrm{p}_x+\frac{1}{2}(\mathrm{p}_{0,\mathrm{H},2}-\mathrm{p}_{0,\mathrm{H},1})]\lvert\alpha\rangle$ $-i\sqrt{\tfrac{2}{3}}[\frac{1}{\sqrt{2}}\mathrm{p}_y+\frac{1}{2}(\mathrm{p}_{y,\mathrm{H},1}+\mathrm{p}_{y,\mathrm{H},2})]\lvert\alpha\rangle\}$	
$\lvert\phi_3 i\rangle_{\mathrm{L}}$	$\frac{1}{\sqrt{6}}\{[\mathrm{p}_{0,\mathrm{H},2}-\mathrm{p}_{0,\mathrm{H},1}-i(\mathrm{p}_{y,\mathrm{H},1}+\mathrm{p}_{y,\mathrm{H},2})]\lvert\alpha\rangle+[\mathrm{p}_{x,\mathrm{H},1}-\mathrm{p}_{x,\mathrm{H},2}]\lvert\beta\rangle\}$	
$\lvert\phi_4 i\rangle_{\mathrm{L}}$	$\frac{1}{\sqrt{2}}(\mathrm{p}_{x,\mathrm{H},1}+\mathrm{p}_{x,\mathrm{H},2})\lvert\alpha\rangle$	
$\lvert\phi_5 i\rangle_{\mathrm{L}}$	$\frac{1}{\sqrt{2}}(\mathrm{p}_{z,\mathrm{H},1}+\mathrm{p}_{z,\mathrm{H},2})\lvert\beta\rangle$	
$\lvert\phi_6 i\rangle_{\mathrm{L}}$	$\frac{1}{\sqrt{2}}(\mathrm{p}_{y,\mathrm{H},1}-\mathrm{p}_{y,\mathrm{H},2})\lvert\beta\rangle$	
$\lvert\phi_7 i\rangle_{\mathrm{L}}$	$S_2\frac{1}{\sqrt{2}}\{[\frac{1}{\sqrt{2}}\mathrm{p}_0+\frac{1}{2}(\mathrm{p}_{x,\mathrm{H},1}-\mathrm{p}_{x,\mathrm{H},2})]\lvert\beta\rangle+[\frac{1}{\sqrt{2}}\mathrm{p}_x-\frac{1}{2}(\mathrm{p}_{0,\mathrm{H},2}-\mathrm{p}_{0,\mathrm{H},1})]\lvert\alpha\rangle$	
$\lvert\phi_8 i\rangle_{\mathrm{L}}$	$S_2\{\frac{1}{\sqrt{6}}[\frac{1}{\sqrt{2}}\mathrm{p}_0+\frac{1}{2}(\mathrm{p}_{x,\mathrm{H},1}-\mathrm{p}_{x,\mathrm{H},2})]\lvert\beta\rangle-\frac{1}{\sqrt{6}}[\frac{1}{\sqrt{2}}\mathrm{p}_x-\frac{1}{2}(\mathrm{p}_{0,\mathrm{H},2}-\mathrm{p}_{0,\mathrm{H},1})]\lvert\alpha\rangle$ $-i\sqrt{\tfrac{2}{3}}[\frac{1}{\sqrt{2}}\mathrm{p}_y-\frac{1}{2}(\mathrm{p}_{y,\mathrm{H},1}+\mathrm{p}_{y,\mathrm{H},2})]\lvert\alpha\rangle\}$	

† In the limit of small overlap F is defined by (7.7 b)}.

(c) *The molecular geometry*

The calculation presented above shows that out of the eight molecular orbitals having eigenvalue i of $\hat{\mathrm{H}}_{z,\mathrm{t}}$, two ($|\phi_1 i\rangle$ and $|\phi_2 i\rangle$) are fully bonding, two ($|\phi_7 i\rangle$ and $|\phi_8 i\rangle$) are fully anti-bonding while the remaining four ($|\chi_{\mathrm{H},1}\rangle$, $|\chi_{\mathrm{H},2}\rangle$, $|\chi_{\mathrm{H},3}\rangle$ and $|\phi_3 i\rangle$) are non-bonding orbitals located entirely on the halogens.

A more complicated calculation presented in Appendix 8 shows that for every Hal–E–Hal bond angle there are still four non-bonding orbitals located entirely on the halogens, of $\hat{\mathrm{H}}_{z,\mathrm{t}}$ eigenvalue i, even if the resonance integrals $F_{\parallel}$ and $F_{\perp}$, defined as

$$\left.\begin{aligned} F_{\parallel} &= \epsilon_{\mathrm{v}}\langle \mathrm{p}_{\parallel,\mathrm{H}}|\mathrm{p}_{\parallel}\rangle+\langle \mathrm{p}_{\parallel,\mathrm{H}}|\hat{V}'_{\mathrm{pot}}|\mathrm{p}_{\parallel}\rangle,\\ F_{\perp} &= \epsilon_{\mathrm{v}}\langle \mathrm{p}_{y,\mathrm{H},1}|\mathrm{p}_y\rangle+\langle \mathrm{p}_{y,\mathrm{H},1}|\hat{V}'_{\mathrm{pot}}|\mathrm{p}_y\rangle,\end{aligned}\right\} \tag{7.12}$$

for pairs of orbitals aligned parallel and perpendicular to the E–Hal bonds are not the same. This calculation also shows that for any bond angle there are still two bonding and two anti-bonding orbitals having $\hat{H}_{z,t}$ eigenvalue i and that the bonding characteristics are independent of the bond angle if the two resonance integrals $F_{\parallel}$ and $F_{\perp}$ are taken to be equal. Since the eight molecular orbitals having eigenvalue $-i$ of $\hat{H}_{z,t}$ can be generated from the eight having $\hat{H}_{z,t}$-eigenvalue i by means of (2.18), it follows that there are four bonding orbitals and eight halogen non-bonding orbitals for all bond angles. Since eight of the twelve valence electrons are accommodated in the halogen non-bonding orbitals leaving four to occupy the fully bonding molecular orbitals, it follows that the order of each p–Hal bond is unity for all bond angles if the distinction between σ and π bonding is not considered. Although it is not possible to predict the equilibrium geometry, the results strongly suggest that the potential energy curve for the bending of the molecule will be shallow. The detailed form of the potential will be determined not by the primary bonding properties of the valence orbitals but by other energetically smaller factors such as the difference between the strengths of σ and π bonds, the behaviour of the outer core orbitals on the central atom, non-bonded repulsions between the end atoms or dispersion forces. Examination of these factors is outside the scope of this paper. It should be pointed out that Walsh diagrams only predict AB_2 molecules containing 13–16 valence electrons to be bent if the s orbital on the central atom is considered.

The prediction that the equilibrium bond angle is not determined by the primary bonding properties of the valence orbitals, with the consequence that the bending potential is predicted to be shallow, is interesting because this situation does not seem to arise in the experimentally known part of the periodic table. However, the results of this section do show that relativity is not predicted to destabilize purely covalently bound $E(Hal)_2$ systems in which the heavy element E has two valence electrons occupying p Dirac–Fock atomic orbitals.

8. Bonding between superheavy elements

(a) *The Kappa valence method*

The bond between the j–j coupled ground states of two heavy elements (A and B) each having a single $\bar{\text{p}}$ or p valence electron is described in the Kappa valence method by the Kappa valence wavefunction

$$|\psi_{\kappa\mathrm{v}\eta}\rangle = S_{\eta}\hat{\mathscr{A}}[|\mathrm{core_A}\rangle|\mathrm{core_B}\rangle \tfrac{1}{\sqrt{2}}(|\mathrm{v_A}\,\tfrac{1}{2}\rangle|\mathrm{v_B}\,-\tfrac{1}{2}\rangle \mp \eta|\mathrm{v_A}\,-\tfrac{1}{2}\rangle|\mathrm{v_B}\,\tfrac{1}{2}\rangle)], \qquad (8.1)$$

having $\eta = 1$. Here $|\mathrm{core_A}\rangle$ and $|\mathrm{core_B}\rangle$ are Hartree products of the type (6.8) constituting the cores of the elements A and B respectively and S_{η} is the normalization constant. The negative sign is taken in (8.1) if $|\mathrm{v_A}\rangle$ and $|\mathrm{v_B}\rangle$ are both $\bar{\text{p}}$ or both p orbitals, the positive sign is taken otherwise, thus ensuring by virtue of the relations (2.29) and (2.30) that $|\psi_{\kappa\mathrm{v}\eta}\rangle$ is symmetric under $\hat{H}_{x,T}$ and $\hat{H}_{y,T}$ if $\eta = 1$ and that it is antisymmetric under these two operators if $\eta = -1$. Furthermore, the relation (2.31) shows that if the atoms A and B are identical, the function (8.1) is symmetric under $\hat{H}_{z,T}$ if $\eta = 1$ and antisymmetric under $\hat{H}_{z,T}$ if $\eta = -1$. Analogously to the wavefunction (3.1), the ground state of the molecule is described by the function (8.1) having $\eta = 1$, while the case $\eta = -1$ describes an excited state.

Application of the first two stages of the four-step process (§3 (*a*)) of investigating the bonding properties of a Kappa valence wavefunction shows that the interaction energy predicted by (8.1) is given by

$$\begin{aligned}E_{\mathrm{int},\eta} = {} & S_\eta^2(\langle \mathrm{v_A}\tfrac{1}{2}|\hat{V}_{\mathrm{NB}}+\hat{V}_{\mathrm{DFB}}|\mathrm{v_A}\tfrac{1}{2}\rangle+\langle \mathrm{v_B}\tfrac{1}{2}|\hat{V}_{\mathrm{NA}}+\hat{V}_{\mathrm{DFA}}|\mathrm{v_B}\tfrac{1}{2}\rangle\\ & \pm\eta\langle \mathrm{v_A}\tfrac{1}{2}|\mathrm{v_B}\tfrac{1}{2}\rangle\langle \mathrm{v_B}-\tfrac{1}{2}|\hat{V}_{\mathrm{NA}}+\hat{V}_{\mathrm{DFA}}+\hat{V}_{\mathrm{NB}}+\hat{V}_{\mathrm{DFB}}|\mathrm{v_A}-\tfrac{1}{2}\rangle\\ & +\langle \mathrm{v_A}\tfrac{1}{2}\mathrm{v_B}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{v_A}\tfrac{1}{2}\mathrm{v_B}-\tfrac{1}{2}\rangle-\langle \mathrm{v_A}\tfrac{1}{2}\mathrm{v_B}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{v_B}-\tfrac{1}{2}\mathrm{v_A}\tfrac{1}{2}\rangle\\ & \mp\eta\langle \mathrm{v_A}\tfrac{1}{2}\mathrm{v_B}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{v_A}-\tfrac{1}{2}\mathrm{v_B}\tfrac{1}{2}\rangle\pm\eta\langle \mathrm{v_A}\tfrac{1}{2}\mathrm{v_B}-\tfrac{1}{2}|r_{12}^{-1}|\mathrm{v_B}\tfrac{1}{2}\mathrm{v_A}-\tfrac{1}{2}\rangle)+R^{-1}, \qquad (8.2a)\end{aligned}$$

$$S_\eta = (1+\eta\langle \mathrm{v_A}\tfrac{1}{2}|\mathrm{v_B}\tfrac{1}{2}\rangle^2)^{-\frac{1}{2}}. \qquad (8.2b)$$

Here $\hat{V}_{\mathrm{DF\mu}}$ is the Dirac–Fock potential due to the core of atom μ while $\hat{V}_{\mathrm{N\mu}}$ is the corresponding nuclear potential. The result (8.2*a*), which has the form (3.8) expected for the interaction energy predicted by a Kappa valence wavefunction, is simplified (stage 3) by expressing the large components of the valence orbitals in terms of purely spatial functions through (3.9) and neglecting the valence orbital small components. Thus introducing the potential $\hat{V}_\mu$ (μ = A, B) defined by (3.10*c*), due to the nucleus plus the core of atom μ, (8.2*a*) becomes, after using the relations (3.5) and (3.9),

$$\begin{aligned}E_{\mathrm{int},\eta} = {} & S_\eta^2\llbracket a_{\mathrm{A}}\langle \mathrm{p_{0,A}}|\hat{V}_{\mathrm{B}}|\mathrm{p_{0,A}}\rangle+(1-a_{\mathrm{A}})\langle \mathrm{p_{1,A}}|\hat{V}_{\mathrm{B}}|\mathrm{p_{1,A}}\rangle+a_{\mathrm{B}}\langle \mathrm{p_{0,B}}|\hat{V}_{\mathrm{A}}|\mathrm{p_{0,B}}\rangle\\ & +(1-a_{\mathrm{B}})\langle \mathrm{p_{1,B}}|\hat{V}_{\mathrm{A}}|\mathrm{p_{1,B}}\rangle+R^{-1}+\eta\{\pm(a_{\mathrm{A}}a_{\mathrm{B}})^{\frac{1}{2}}\langle \mathrm{p_{0,A}}|\mathrm{p_{0,B}}\rangle\\ & +[(1-a_{\mathrm{A}})(1-a_{\mathrm{B}})]^{\frac{1}{2}}\langle \mathrm{p_{1,A}}|\mathrm{p_{1,B}}\rangle\}\times\{\pm(a_{\mathrm{A}}a_{\mathrm{B}})^{\frac{1}{2}}\langle \mathrm{p_{0,A}}|\hat{V}_{\mathrm{A}}+\hat{V}_{\mathrm{B}}+R^{-1}|\mathrm{p_{0,B}}\rangle\\ & +[(1-a_{\mathrm{A}})(1-a_{\mathrm{B}})]^{\frac{1}{2}}\langle \mathrm{p_{1,A}}|\hat{V}_{\mathrm{A}}+\hat{V}_{\mathrm{B}}+R^{-1}|\mathrm{p_{1,B}}\rangle\}\\ & +a_{\mathrm{A}}a_{\mathrm{B}}\langle \mathrm{p_{0,A}p_{0,B}}|r_{12}^{-1}(1+\eta\hat{\mathrm{P}}_{12})|\mathrm{p_{0,A}p_{0,B}}\rangle\\ & +a_{\mathrm{A}}(1-a_{\mathrm{B}})\langle \mathrm{p_{0,A}p_{1,B}}|r_{12}^{-1}(1-\hat{\mathrm{P}}_{12})|\mathrm{p_{0,A}p_{1,B}}\rangle\\ & +(1-a_{\mathrm{A}})a_{\mathrm{B}}\langle \mathrm{p_{1,A}p_{0,B}}|r_{12}^{-1}(1-\hat{\mathrm{P}}_{12})|\mathrm{p_{1,A}p_{0,B}}\rangle\\ & +(1-a_{\mathrm{A}})(1-a_{\mathrm{B}})(\langle \mathrm{p_{1,A}p_{-1,B}}|r_{12}^{-1}|\mathrm{p_{1,A}p_{-1,B}}\rangle+\eta\langle \mathrm{p_{1,A}p_{-1,B}}|r_{12}^{-1}|\mathrm{p_{1,B}p_{-1,A}}\rangle)\\ & \pm 2[a_{\mathrm{A}}a_{\mathrm{B}}(1-a_{\mathrm{A}})(1-a_{\mathrm{B}})]^{\frac{1}{2}}[\eta\langle \mathrm{p_{0,A}p_{1,B}}|r_{12}^{-1}|\mathrm{p_{0,B}p_{1,A}}\rangle-\langle \mathrm{p_{0,A}p_{0,B}}|r_{12}^{-1}|\mathrm{p_{-1,B}p_{1,A}}\rangle\\ & -\eta\langle \mathrm{p_{0,A}p_{1,B}}|r_{12}^{-1}|\mathrm{p_{1,A}p_{0,B}}\rangle-\eta\langle \mathrm{p_{0,A}p_{0,B}}|r_{12}^{-1}|\mathrm{p_{-1,A}p_{1,B}}\rangle]\rrbracket, \qquad (8.3)\end{aligned}$$

where a_{A} and a_{B} are the analogues for atoms A and B of the quantity a defined after (3.10). By expressing the complex p orbitals in terms of p_x and p_y, it follows that $\langle \mathrm{p_{0,A}p_{0,B}}|r_{12}^{-1}|\mathrm{p_{-1,A}p_{1,B}}\rangle = -\langle \mathrm{p_{0,A}p_{1,B}}|r_{12}^{-1}|\mathrm{p_{1,A}p_{0,B}}\rangle$ which shows that the last two terms in (8.3) sum to zero. This result is useful because the remainder of (8.3) can be illuminatingly expressed in terms of the quantities X_{int}, (6.43), and the interaction energies predicted by non-orthogonal Heitler–London singlet and triplet, and orthogonal triplet wavefunctions. The results for the functions (8.1) having η = 1 and -1 respectively are found after (6.41) to be

$$\begin{aligned}E_{\mathrm{int},1} = {} & S_1^2\{a_{\mathrm{A}}a_{\mathrm{B}}\,{}^{1,\mathrm{N}}H_{\mathrm{int}}(\mathrm{p_{0,A}},\mathrm{p_{0,B}},V_{\mathrm{A}},V_{\mathrm{B}})+(1-a_{\mathrm{A}})(1-a_{\mathrm{B}})\,{}^{1,\mathrm{N}}H_{\mathrm{int}}(\mathrm{p_{1,A}},\mathrm{p_{1,B}},V_{\mathrm{A}},V_{\mathrm{B}})\\ & \pm[a_{\mathrm{A}}a_{\mathrm{B}}(1-a_{\mathrm{A}})(1-a_{\mathrm{B}})]^{\frac{1}{2}}[X_{\mathrm{int}}(\mathrm{p_{0,A}},\mathrm{p_{0,B}},\mathrm{p_{1,A}},\mathrm{p_{1,B}},V_{\mathrm{A}},V_{\mathrm{B}})\\ & -2\langle \mathrm{p_{0,A}p_{0,B}}|r_{12}^{-1}|\mathrm{p_{-1,B}p_{1,A}}\rangle]+a_{\mathrm{A}}(1-a_{\mathrm{B}})\,{}^{3,0}H_{\mathrm{int}}(\mathrm{p_{0,A}},\mathrm{p_{1,B}},V_{\mathrm{A}},V_{\mathrm{B}})\\ & +(1-a_{\mathrm{A}})a_{\mathrm{B}}\,{}^{3,0}H_{\mathrm{int}}(\mathrm{p_{1,A}},\mathrm{p_{0,B}},V_{\mathrm{A}},V_{\mathrm{B}})\}, \qquad (8.4a)\end{aligned}$$

$$\begin{aligned}E_{\mathrm{int},-1} = {} & S_{-1}^2\{a_{\mathrm{A}}a_{\mathrm{B}}\,{}^{3,\mathrm{N}}H_{\mathrm{int}}(\mathrm{p_{0,A}},\mathrm{p_{0,B}},V_{\mathrm{A}},V_{\mathrm{B}})+(1-a_{\mathrm{A}})(1-a_{\mathrm{B}})\,{}^{3,\mathrm{N}}H_{\mathrm{int}}(\mathrm{p_{1,A}},\mathrm{p_{1,B}},V_{\mathrm{A}},V_{\mathrm{B}})\\ & \mp[a_{\mathrm{A}}a_{\mathrm{B}}(1-a_{\mathrm{A}})(1-a_{\mathrm{B}})]^{\frac{1}{2}}[X_{\mathrm{int}}(\mathrm{p_{0,A}},\mathrm{p_{0,B}},\mathrm{p_{1,A}},\mathrm{p_{1,B}},V_{\mathrm{A}},V_{\mathrm{B}})\\ & -2\langle \mathrm{p_{0,A}p_{0,B}}|r_{12}^{-1}|\mathrm{p_{-1,B}p_{1,A}}\rangle]+a_{\mathrm{A}}(1-a_{\mathrm{B}})\,{}^{3,0}H_{\mathrm{int}}(\mathrm{p_{0,A}},\mathrm{p_{1,B}},V_{\mathrm{A}},V_{\mathrm{B}})\\ & +(1-a_{\mathrm{A}})a_{\mathrm{B}}\,{}^{3,0}H_{\mathrm{int}}(\mathrm{p_{1,A}},\mathrm{p_{0,B}},V_{\mathrm{A}},V_{\mathrm{B}})\}. \qquad (8.4b)\end{aligned}$$

The quantity $\langle p_{0,A}\,p_{0,B}|r_{12}^{-1}|p_{-1,B}\,p_{1,A}\rangle$ will be positive but will be much smaller than the X_{int}-term and does not therefore affect the qualitative features of the bonding. The result (8.4*a*) shows, in the small overlap limit for which $S_1 = 1$, that both p̄–p̄ and the description (8.1) of p–p bonds consist of $\frac{5}{9}$ of a non-orthogonal Heitler–London singlet bond and of $\frac{4}{9}$ of an orthogonal triplet one, but that both p̄–p̄ and p–p bonds are destabilized by $\frac{2}{9}$ of an X_{int} term. These results predict the bond orders of both these bonds to be $\frac{1}{3}$ if a single term X_{int} is taken to contribute -2 to the bond order while the order of an orthogonal triplet bond is taken to be $\frac{1}{2}$ as discussed previously. Although p̄–p̄ bonds are predicted to be weak because they contain a substantial destabilizing component, the result (8.4*a*) shows that p̄–p bonds are stabilized by the X_{int}-term. The contribution $(\frac{4}{9})$ of this stabilizing term to the order of a p̄–p bond taken in conjunction with the $\frac{4}{9}$ non-orthogonal Heitler–London singlet and $\frac{5}{9}$ orthogonal triplet character of such a bond exhibited by (8.4*a*) shows that the total order of a p̄–p bond is $\frac{21}{18}$. This result clearly shows that the bond between an element contains a single p̄ valence electron, and one containing a single p valence electron is not destabilized by relativity.

The prediction that p–p bonds are weak, having an order of $\frac{1}{3}$, applies only to the wavefunction (8.1) but does not apply to the bond that would actually be formed between two elements each having a single p valence electron. This distinction arises for p–p bonds but not p̄–p̄ or p̄–p ones because for two elements each containing one valence p electron there exists a mode of bonding different from that described by the wavefunction (8.1). The Kappa valence wavefunction

$$|\psi_{\kappa v\pi}\rangle = S_\pi\hat{\mathscr{A}}[|\text{core}_A\rangle|\text{core}_B\rangle\tfrac{1}{\sqrt{2}}(|p_A\tfrac{3}{2}\rangle|p_B-\tfrac{3}{2}\rangle-|p_A-\tfrac{3}{2}\rangle|p_B\tfrac{3}{2}\rangle)], \tag{8.5}$$

is readily shown, by using the large components (3.9), to describe the formation of a pure π bond whose order is unity. Hence p–p bonds are not predicted to be significantly destabilized by relativity.

The Kappa valence method predicts the orders of both p̄–p bonds and of the bond (6.35) between either a p̄ or a p orbital and a halogen in its optimal valence state to be greater than unity. The results of the Kappa valence description of the bond between two heavy elements and the meaning of a prediction of an order greater than unity for a bond formed from just two electrons are illuminated by introducing the four non-relativistic wavefunctions

$$\left.\begin{aligned}|{}^1\Sigma_\sigma\rangle &= S_\sigma\hat{\mathscr{A}}[|\text{core}_A^{NR}\rangle|\text{core}_B^{NR}\rangle|p_{0,A}\,p_{0,B}\rangle\tfrac{1}{\sqrt{2}}|\alpha\beta-\beta\alpha\rangle],\\ |\Sigma_\pi\rangle &= S_\pi\hat{\mathscr{A}}[|\text{core}_A^{NR}\rangle|\text{core}_B^{NR}\rangle\tfrac{1}{\sqrt{2}}(|p_{1,A}\,p_{-1,B}\rangle|\beta\alpha\rangle-|p_{-1,A}\,p_{1,B}\rangle|\alpha\beta\rangle)],\\ |{}^3\Pi\rangle &= \hat{\mathscr{A}}[|\text{core}_A^{NR}\rangle|\text{core}_B^{NR}\rangle\tfrac{1}{\sqrt{2}}(|p_{0,A}\,p_{-1,B}\rangle|\alpha\alpha\rangle-|p_{0,A}\,p_{1,B}\rangle|\beta\beta\rangle)],\\ |{}^3\Pi'\rangle &= \hat{\mathscr{A}}[|\text{core}_A^{NR}\rangle|\text{core}_B^{NR}\rangle\tfrac{1}{\sqrt{2}}(|p_{1,A}\,p_{0,B}\rangle|\beta\beta\rangle-|p_{-1,A}\,p_{0,B}\rangle|\alpha\alpha\rangle)].\end{aligned}\right\} \tag{8.6}$$

If the differences between the radial parts of $|v_\mu\rangle_L$ and those of $|v_\mu\rangle$ are neglected, the large components of $|\psi_{\kappa v1}\rangle$ can be written

$$|\psi_{\kappa v1}\rangle_L = -\{e_A e_B|{}^1\Sigma_\sigma\rangle+[(1-a_A)(1-a_B)]^{\frac{1}{2}}|\Sigma_\pi\rangle+e_A(1-a_B)^{\frac{1}{2}}|{}^3\Pi\rangle+(1-a_A)^{\frac{1}{2}}e_B|{}^3\Pi'\rangle\} \tag{8.7}$$

where e_μ is $-\frac{1}{\sqrt{3}}$ if atom μ has a p̄ valence orbital while e_μ is $\sqrt{\frac{2}{3}}$ if this atom has a p valence orbital. The two functions $|{}^1\Sigma_\sigma\rangle$ and $|\Sigma_\pi\rangle$, the latter being the Σ-function built from π valence orbitals, are the source of the Heitler–London singlet contributions (the first two terms in (8.4*a*)) to the bonding described by $|\psi_{\kappa v1}\rangle$, while $|{}^3\Pi\rangle$ and $|{}^3\Pi'\rangle$ are responsible for the orthogonal-triplet contribution (the last two terms in (8.4*a*)). The X_{int}-term is seen to arise as the interatomic contribution to the matrix element between $|{}^3\Pi\rangle$ and $|{}^3\Pi'\rangle$, while $\langle p_{0,A}\,p_{0,B}|r_{12}^{-1}|p_{-1,A}\,p_{1,B}\rangle$ arises similarly from $|{}^1\Sigma_\sigma\rangle$ and $|\Sigma_\pi\rangle$. The terms inside the two pairs of square brackets in (8.4*a*) are thus seen to constitute a resonance contribution, the prediction of bond orders greater than unity being thus explained. Since bond orders greater than unity are predicted by non-relativistic multi-structure valence bond theory, it is doubtful whether such predictions indicate any strength beyond that of a normal covalent single bond.

(*b*) *The relativistic molecular orbital description*

The bond formed between the *j–j* coupled ground state of two superheavy elements each of which has a single valence p̄ or p electron is perhaps described more simply and transparently by relativistic molecular orbital theory which yields the same predictions as the Kappa valence method. The results (2.18) and $\hat{H}^2_{q,t} = -1$ show that a relativistic molecular orbital wavefunction symmetric under both $\hat{H}_{x,T}$ and $\hat{H}_{y,T}$ and which describes purely covalent p̄–p̄, p–p or p̄–p bonding is

$$|\psi_{M0,m}\rangle = \hat{\mathscr{A}}[|\mathrm{core_A}\rangle|\mathrm{core_B}\rangle|\phi m\rangle|\phi-m\rangle]. \tag{8.8}$$

Here $|\phi m\rangle$ and $|\phi-m\rangle$ are the two bonding orbitals, with the label m on $|\psi_{M0,m}\rangle$ denoting the positive m_j quantum number of the first of these two orbitals. For both p̄–p̄ and p̄–p bonds m takes the value $\frac{1}{2}$, while there are two orthogonal multi-electron wavefunctions $|\psi_{M0,\frac{1}{2}}\rangle$ and $|\psi_{M0,\frac{3}{2}}\rangle$ if both atoms A and B have a single valence p Dirac–Fock atomic orbital. The qualitative features of the bonding are revealed as discussed in §3(*c*i) by expanding $|\phi m\rangle$ in just the two valence Dirac–Fock atomic orbitals of the same m_j quantum number. Thus

$$|\phi m\rangle = \tfrac{1}{\sqrt{2}}S_m\,(|\mathrm{v_A}m\rangle \pm |\mathrm{v_B}m\rangle), \tag{8.9}$$

where the upper (positive) sign is taken for $m = \frac{3}{2}$ for the p̄–p̄ and p̄–p cases, while the lower (negative) sign is taken if both $|\mathrm{v_A}\tfrac{1}{2}\rangle$ and $|\mathrm{v_B}\tfrac{1}{2}\rangle$ are p orbitals. In (8.9) S_m is a normalization constant which becomes unity in the limit of negligible overlap.

The expressions (3.9) show that for the description of p̄–p̄ and p–p bonds provided by setting $m = \frac{1}{2}$ in the wavefunction (8.8), the large components of the bonding molecular orbital (8.9) are

$$|\phi\tfrac{1}{2}\rangle_\mathrm{L} = S_m[\sqrt{a}\,\tfrac{1}{\sqrt{2}}\,|\mp(\mathrm{p_{0,A}}-\mathrm{p_{0,B}})\alpha\rangle + (1-a)^{\frac{1}{2}}\,\tfrac{1}{\sqrt{2}}\,|(\mathrm{p_{1,A}}+\mathrm{p_{1,B}})\beta\rangle]. \tag{8.10}$$

This result shows that p̄–p̄ bonds ($a = \frac{1}{3}$) have $\frac{1}{3}\sigma$ anti-bonding and $\frac{2}{3}\pi$ bonding character and hence in agreement with the Kappa valence method that the bond order is predicted to be $\frac{1}{3}$. This shows that the bonding between two heavy elements each having a single valence p̄ electron for which the p̄ → p excitation energy is large are very substantially destabilized by relativity.

For the description of p–p bonding provided by the wavefunction (8.8) with $m = \frac{1}{2}$, the large components (8.10) of the bonding molecular orbital show that this orbital is $\frac{2}{3}\sigma$ bonding and $\frac{1}{3}\pi$ anti-bonding and hence that this description predicts a bond order of $\frac{1}{3}$. However, the actual bonding between two elements each containing a single electron occupying a Dirac–Fock p orbital is not destabilized by anti-bonding components because for these systems there exists an alternative mode of bonding. The large components of the bonding molecular orbital $|\phi\tfrac{3}{2}\rangle$ are given by

$$|\phi\tfrac{3}{2}\rangle_\mathrm{L} = \tfrac{1}{\sqrt{2}}\,S_\pi|(\mathrm{p_{1,A}}+\mathrm{p_{1,B}})\alpha\rangle, \tag{8.11}$$

which shows in agreement with the Kappa valence method that p–p bonds are purely π in character, having unit bond order. Hence relativity is not predicted substantially to destabilize p–p bonds. For $(\mathrm{E}115)_2$ the only reason for supposing that the bond might be weaker than a normal covalent σ bond is that the overlap between the outer-core $7\bar{p}^2$ closed subshells of the two atoms might introduce a non-negligible repulsive term into the interaction energy for the fairly small internuclear separations necessary for significant overlap of the $p_\pi(|p\tfrac{3}{2}\rangle)$ valence orbitals.

For p̄–p bonds the large components of the bonding molecular orbital are

$$|\phi\tfrac{1}{2}\rangle_L = S_m[\tfrac{1}{\sqrt{2}}\,|(-\tfrac{1}{\sqrt{3}}\,p_{0,A}+\sqrt{\tfrac{2}{3}}\,p_{0,B})\,\alpha\rangle+\tfrac{1}{\sqrt{2}}\,|(\sqrt{\tfrac{2}{3}}\,p_{1,A}+\tfrac{1}{\sqrt{3}}\,p_{1,B})\,\beta\rangle], \qquad (8.12)$$

where $|v_A\rangle$ is a p̄ orbital and $|v_B\rangle$ is a p one. Although there may be a slight ambiguity in the prediction of the order of p̄–p bonds by examining (8.12), it seems clear that this order is close to unity. With the simplest and probably dubious assumption that the orbital $p_{\phi,m}$ $(= \tfrac{1}{\sqrt{3}}(p_{m,\mu}+\sqrt{2}\,p_{m,\mu'}),\ \mu = A \text{ or } B)$ is fully bonding, the bond order is predicted to be unity because (8.12) would then be interpreted as an equal mixture of a fully bonding σ and a fully bonding π molecular orbital. The assumption that the orbital $p_{\phi,m}$ has unit order is probably incorrect because in the limit $c_A = 1$ and $c_B = 0$ for the more general orbital $(c_A\,p_{0,A}+c_B\,p_{0,B})$ of which $p_{\phi,m}$ is a particular case, the large components (8.12) would become, for purely covalent bonding, $\tfrac{1}{\sqrt{2}}|-p_{0,A}\,\alpha+p_{1,B}\,\beta\rangle$ which certainly does not correspond to a bond of unit order. However if $p_{\phi,0}$ is expressed as a linear combination of the orbitals σ and σ* defined through

$$\left.\begin{aligned}\sigma &= S_0\,\tfrac{1}{\sqrt{2}}\,(-p_{0,A}+p_{0,B}),\\ \sigma^* &= S_0^*\,\tfrac{1}{\sqrt{2}}\,(p_{0,A}+p_{0,B}),\end{aligned}\right\} \qquad (8.13)$$

which are regarded as fully bonding and fully anti-bonding respectively, so that with the neglect of overlap

$$p_{\phi,0} = \tfrac{1}{\sqrt{6}}\,[(1+\sqrt{2})\sigma+(\sqrt{2}-1)\sigma^*], \qquad (8.14)$$

the bond order is predicted to be $\tfrac{1}{6}[(1+\sqrt{2})^2-(\sqrt{2}-1)^2] = \tfrac{2\sqrt{2}}{3}$ if the π component of (8.12) is analogously decomposed into $\tfrac{1}{\sqrt{2}}(p_{1,A}+p_{1,B})$ and $\tfrac{1}{\sqrt{2}}(p_{1,A}-p_{1,B})$. Since the bonding (8.12) is purely covalent and the entire electron density contributes to the bonding, unlike for the p̄–H and p–H bonds examined in §3(*c*ii), it is reasonable to determine the bond order from (8.12) by comparing the coefficient multiplying the overlap density in $p_{\varphi,0}$, shown in §3(*c*i) to be primarily responsible for the bonding, with the coefficient ($\tfrac{1}{2}$) multiplying the overlap density in the fully bonding orbital σ (8.13). After applying the same argument to the π component of (8.12), this approach predicts the same bond order $\tfrac{2\sqrt{2}}{3}$ as that calculated by expanding $|\phi\tfrac{1}{2}\rangle_L$ according to (8.14). Although the molecular orbital and Kappa valence methods do not predict the identical bond order, both predictions are sufficiently close to unity that it can be concluded that p̄–p bonds are not substantially destabilized by relativity.

The nature of the bonding between two heavy elements deduced in this section can be used to discuss the cohesion of the elements (E113 and E115) containing a single valence electron occupying a p̄ or p Dirac–Fock atomic orbital. Since the p̄ → p excitation energies (see paper I) are large compared with the cohesive energies of the elements, it can be predicted that the electronic structures of the solids will be determined by the bonding characteristics of the *j*–*j* coupled ground states of the atoms. If the energy bands in the solid are regarded as formed from the overlap of the valence atomic orbitals, it follows that E113 may be even more volatile than predicted by simple extrapolation of the boiling points and heats of vapourization down group IIIB of the Periodic Table because the results of the previous paragraphs show that overlap of two p̄ orbitals yields a weak bond. Such high volatility is not predicted for E115 because overlap of $|\mathrm{p}\tfrac{3}{2}\rangle$ atomic orbitals yields a fully bonding π orbital. This suggests that it might be predicted that the structure of E115 would consist of chains of atoms bound by the partial filling of energy bands constructed from the overlap of both $|\mathrm{p}\tfrac{3}{2}\rangle$ and $|\mathrm{p}-\tfrac{3}{2}\rangle$ atomic orbitals. The interaction between the chains would be much weaker because consideration of two such parallel chains shows that the interaction between them contains equal numbers of bonding and anti-bonding (in-phase and out-of-phase overlaps of the large components of the atomic orbitals) interactions. The predicted weakness of the cohesion of elemental E113 coupled with the approximately fully bonding character of the bond (8.12) formed by the overlap of a $\bar{\mathrm{p}}$ with a p Dirac–Fock atomic orbital further suggests that E113 and E115 would form a stable 1:1 alloy.

9. Conclusion

It has been shown by using both the Kappa valence and the relativistic molecular orbital approaches that the ground relativistic configuration of an element containing a single valence $\bar{\mathrm{p}}$ or p electron can form a stable covalent bond without invoking a valence state in which electrons are partially promoted from $\bar{\mathrm{p}}$ into p orbitals. Although the two approaches predict different fractions of the bond to be of the normal singlet covalent type, they do agree in predicting that the overall orders of purely covalent $\bar{\mathrm{p}}$–H and p–H bonds are $\frac{2}{3}$ and $\frac{5}{6}$ respectively in the limit of small overlap. Hence such bonds are predicted to be weakened only moderately compared with normal covalent σ bonds.

The Kappa valence method predicts that $\bar{\mathrm{p}}$–H and p–H bonds are partly composed of a normal covalent σ bond and partly of the triplet bond formed by the interaction of two electrons occupying orthogonal orbitals. This method further predicts that the bond formed between a heavy element and a group of rather different electronegativity may be weakened by relativity more than a purely covalent $\bar{\mathrm{p}}$–H or a p–H bond because only the non-orthogonal Heitler–London singlet portion of such a bond can be stabilized by ionic–covalent resonance.

Both the Kappa valence and relativistic molecular orbital methods predict that the ground relativistic configuration of an atom having two electrons occupying p Dirac–Fock atomic orbitals can bind two hydrogen atoms and that the resulting molecule will be bent. With further Huckel-like assumptions relativistic molecular orbital theory predicts the equilibrium bond angle to be 90°. The Kappa valence method also predicts that the bond angle will be 90° and that such bonds will be slightly weaker than the p–H bond formed by an atom having only one valence p electron. Finally it has been shown that a $\bar{\mathrm{p}}^2$ subshell behaves like a closed shell in that it cannot form stable covalent bonds.

Although the bonding between the ground relativistic configuration of a heavy element and hydrogen atoms was considered in detail, it is clear that the conclusions will apply to the bond between such a configuration and any atom or group containing no valence π electrons and a single unpaired electron occupying a σ orbital.

It was shown by using the Kappa valence method that the nature of the purely covalent bonding between the *j–j* coupled ground state of a heavy element having a single valence electron occupying a $\bar{\mathrm{p}}$ or p Dirac–Fock atomic orbital and a group described non-relativistically as containing both a filled shell of valence π orbitals and a single unpaired electron occupying a σ orbital depended strongly on the $\pi \rightarrow \sigma$ excitation energy. If this excitation energy is large it was shown that the π symmetry portion of the large components of the $\bar{\mathrm{p}}$ or p valence orbital of the heavy element introduced a substantial destabilizing anti-bonding component into the interaction. If the heavy element had a single valence p̄ electron this destabilizing contribution is sufficiently large to inhibit the formation of a normal covalent bond although for a heavy element having a single valence p electron the bond is merely predicted to be greatly weakened, having an order of $\frac{1}{3}$. However, if the σ and π orbitals of the free bonded group are degenerate as for a halogen it was shown by both the Kappa valence and relativistic molecular orbital methods that the group would adopt a valence state that eliminated the anti-bonding terms from the interaction to yield a bond of unit order having both a σ and a π symmetry contribution. Finally it was shown for the case where the σ and π orbitals of the free group are degenerate that if the group and the heavy element have different electronegativities the ionic–covalent resonance stabilization will not differ qualitatively from that of the bond in the corresponding non-relativistic system.

Relativistic molecular orbital theory was used to show that the ground manifold of a heavy element containing two valence electrons occupying Dirac–Fock p orbitals could bind covalently two groups each described in non-relativistic theory as having four electrons occupying π orbitals and one electron occupying a σ orbital. It was assumed in this investigation that the σ and π orbitals in the free groups were degenerate. It was predicted, for all bond angles, both that four electrons occupied bonding molecular orbitals and that the orders of the bonds were unity, and hence that the potential energy curve for angle bending would be shallow. The presence of π orbitals degenerate with the σ orbital on the bound group changes the nature of the bonding from that arising when the bound group has only a single σ electron in that neither are the bonds predicted to be significantly weakened nor is an equilibrium bond angle of 90° strongly favoured.

The bonding between the *j–j* coupled ground states of two heavy elements each having a single electron occupying a Dirac–Fock p̄ or p orbital was investigated by using both the Kappa valence and the relativistic molecular orbital methods. Both methods agree in predicting that p̄–p̄ bonds will be weak, having an order of $\frac{1}{3}$, because they contain a substantial anti-bonding component. Both approaches also agree in predicting that p–p bonds will be entirely π in character, having unit order. Both methods further agree in predicting that p̄–p bonds contain equal σ and π contributions and that the bond order is approximately unity. It has therefore been shown that there are no good reasons for believing that either p–p or p̄–p bonds are significantly destabilized by relativity.

This paper has been concerned solely with the purely covalent bonds that can be formed by the ground manifold of a superheavy element if all the orbitals except the most loosely bound one are assumed to be sufficiently contracted that they can be regarded as belonging to the core. The chemistry of superheavy elements can only be predicted by considering all the possible modes of bonding that might be exhibited by such elements. It appears that any such mode can be described as some mixture of three extreme bonding types, namely ionic, relativistic valence bond and Kappa valence. Any quantum chemical calculations on molecules containing superheavy elements that may in future be made might show either that the covalent bonding has a character intermediate between that described by the relativistic valence bond method (full hydridization of the p̄ and p orbitals being assumed to produce orbitals whose large components have pure σ or pure π character) and the Kappa valence method or that the outermost core orbitals play a non-negligible role. However, it should be stressed that the remarks of Coulson (1960) on the limited utility of accurate numbers whether they be obtained from experiment or computation show that the results of any such calculations on compounds containing superheavy elements will need to be interpreted and understood in physical terms. A system covalent bound to pure unhydridized Dirac–Fock atomic orbitals is one of the limiting models needed for comparison with the results of computer calculations. This paper has provided the understanding of this limit which is a necessary prerequisite for its use in understanding the results of such computations. Paper III of this series (in preparation) examines possible compounds formed by superheavy elements by comparing the heats of formation predicted by the ionic model with those predicted by both the relativistic valence bond and the Kappa valence methods, the latter predictions being made from the characteristics of the bonding elucidated here. By this means the chemistry of the 7p series of superheavy elements is predicted.

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APPENDIX 1. THE PHASES OF THE OPERATORS $H_{q,\mathrm{u}}$

The phases of the operators (2.13) are determined by demanding that they satisfy the group multiplication table and therefore obey

$$H_{q,\mathrm{u}} = \beta R_{q,\mathrm{u}}(\pm\pi) \tag{A 1.1}$$

by analogy with the relation

$$\hat{H}_{q,\mathrm{s}} = \hat{I}_{\mathrm{s}}\hat{R}_{q,\mathrm{s}}(\pm\pi) \tag{A 1.2}$$

satisfied by the operators, corresponding, through relations of the type (2.10), to purely spatial symmetry operations. Here $\hat{R}_{q,\mathrm{s}}(\pi)$ is the operator pertaining to a rotation of the coordinate system through an angle $-\pi$ about the q-axis (Brink & Satchler 1962). The operator I_{u} is chosen by convention to be β rather than $-\beta$ or $\pm i\beta$, even though the commutator $[\hat{F}, \hat{I}_{\mathrm{t}}]$ still vanishes for all three of these alternative definitions, because the choice $I_{\mathrm{u}} = \beta$ causes the large components to transform under the Dirac parity operator $\hat{I}_{\mathrm{t}}$ in exactly the same way as non-relativistic wavefunctions do under $\hat{I}_{\mathrm{s}}$. Since it is a standard result that the operator corresponding to a rotation for both space and spin of the coordinates through an angle ϕ about the axis q is $\exp(-\mathrm{i}\hat{l}_q\phi)\exp(-\frac{1}{2}\mathrm{i}\Sigma_q\phi)$ (Brink & Satchler 1962), equation (A 1.1) taken in conjunction with $I_{\mathrm{u}} = \beta$ shows that $H_{q,\mathrm{u}}$ must be defined as $\pm\mathrm{i}\Sigma_q\beta$. The signs of the operators $H_{q,\mathrm{u}}$ are not uniquely defined because (A 1.2) is satisfied with both $\hat{R}_{q,\mathrm{s}}(\pi)$ and $\hat{R}_{q,\mathrm{s}}(-\pi)$. The positive sign $(+\pi)$ will be chosen in (A 1.2) and hence in (A 1.1), the definitions (2.13) thus being fixed.

APPENDIX 2. THE ACTION OF THE OPERATORS $\hat{H}_{x,\mathrm{t}}$ AND $\hat{H}_{y,\mathrm{t}}$ ON THE KETS $|\phi_a m i_{\mathrm{p}} h_z\rangle$

The kets $|\phi_a m i_{\mathrm{p}} h_z\rangle$, (2.17), are not eigenkets of $\hat{H}_{x,\mathrm{t}}$ or $\hat{H}_{y,\mathrm{t}}$ because neither of these two operators commutes with $\hat{j}_z$ or $\hat{H}_{z,\mathrm{t}}$. However, left multiplication of (2.8) by $\hat{H}_{x,\mathrm{t}}$ or $\hat{H}_{y,\mathrm{t}}$ shows that $\hat{H}_{x,\mathrm{t}}|\phi_a m i_{\mathrm{p}} h_z\rangle$ and $\hat{H}_{y,\mathrm{t}}|\phi_a m i_{\mathrm{p}} h_z\rangle$ are eigenkets of $\hat{F}$ degenerate with $|\phi_a m i_{\mathrm{p}} h_z\rangle$.

The action of the operators $\hat{H}_{x,\mathrm{t}}$ and $\hat{H}_{y,\mathrm{t}}$ when expressed in terms of spherical polar coordinates (r, θ, ϕ) is to change ϕ to $\pi-\phi$ and $-\phi$ respectively. It therefore follows by writing $\hat{l}_z$ as $-\mathrm{i}\partial/\partial\phi$ that

$$\hat{H}_{q,\mathrm{s}}^{-1}\hat{l}_z\hat{H}_{q,\mathrm{s}} = -\hat{l}_z \tag{A 2.1}$$

whence, since both Σ_1 and Σ_2 anti-commute with Σ_3, it follows both that

and that

$$\left.\begin{aligned} \hat{H}_{q,\mathrm{t}}^{-1}\hat{j}_z\hat{H}_{q,\mathrm{t}} &= -\hat{j}_z, \\ \hat{H}_{q,\mathrm{t}}^{-1}\hat{H}_{z,\mathrm{t}}\hat{H}_{q,\mathrm{t}} &= -\hat{H}_{z,\mathrm{t}}, \end{aligned}\right\} \quad q = x, y, \tag{A 2.2}$$

where the commutation of all the H_qs is used in the second result. Left-multiplying the eigenvalue equations (2.17a) and (2.17b) for m and h_z by $\hat{H}_{x,\mathrm{t}}$ or $\hat{H}_{y,\mathrm{t}}$ and then invoking (A 2.2) show that

$$\left.\begin{aligned} \hat{j}_z(\hat{H}_{q,\mathrm{t}}|\phi_a m i_{\mathrm{p}} h_z\rangle) &= -m(\hat{H}_{q,\mathrm{t}}|\phi_a m i_{\mathrm{p}} h_z\rangle), & &\text{(A 2.3}a\text{)} \\ \hat{H}_{z,\mathrm{t}}(\hat{H}_{q,\mathrm{t}}|\phi_a m i_{\mathrm{p}} h_z\rangle) &= -h_z(\hat{H}_{q,\mathrm{t}}|\phi_a m i_{\mathrm{p}} h_z\rangle). & &\text{(A 2.3}b\text{)} \end{aligned}\right\} \quad q = x, y.$$

The results (A 2.3) show that $\hat{H}_{x,\mathrm{t}}|\phi_a m i_{\mathrm{p}} h_z\rangle$ and $\hat{H}_{y,\mathrm{t}}|\phi_a m i_{\mathrm{p}} h_z\rangle$, which have already been shown to be eigenkets of $\hat{F}$ degenerate with $|\phi_a m i_{\mathrm{p}} h_z\rangle$, are eigenkets of $\hat{j}_z$ and $\hat{H}_{z,\mathrm{t}}$ of eigenvalues $-m$ and $-h_z$ respectively. These two kets have the same eigenvalues i_{p} of $\hat{I}_{\mathrm{t}}$ as $|\phi_a m i_{\mathrm{p}} h_z\rangle$

because $\hat{\mathrm{I}}_{\mathrm{t}}$ commutes with both $\hat{\mathrm{j}}_z$ and $\hat{\mathrm{H}}_{z,\mathrm{t}}$. The relation $\hat{\mathrm{H}}^{+}_{q,\mathrm{t}}\hat{\mathrm{H}}_{q,\mathrm{t}} = 1$ shows that the two kets $\hat{\mathrm{H}}_{q,\mathrm{t}}|\phi_a m i_{\mathrm{p}} h_z\rangle$ both have unit norm whence it follows from (A 2.3) that they can differ from $|\phi_a - m i_{\mathrm{p}} - h_z\rangle$ by at most a phase factor $\mathrm{e}^{\mathrm{i}\delta_q}$, this establishing the result (2.18).

APPENDIX 3. THE MAGNITUDE OF THE MATRIX ELEMENTS OF THE IONIC COVALENT RESONANCE SECULAR PROBLEM

It is the purpose of this Appendix to present evidence that the difference $(H^{\mathrm{or}}_{22} - E_{\mathrm{int}})$ is greater in magnitude than the off-diagonal element H^{or}_{12} thus justifying the expansion of (3.25) according to (3.26).

The nearest-neighbour interionic separation in a crystal composed of E^+ and H^- ions is greater than that of the isolated ion pair $\mathrm{E}^+\mathrm{H}^-$. Consequently the repulsion arising from the overlapping of the closed electronic shells of E^+ and H^- will be much less than the coulombic attraction at the inter-ionic separation equal to the sum $(r_{\mathrm{E}^+} + r_{\mathrm{H}^-})$ of the ionic radii of E^+ and H^-. If this overlap is neglected the binding energy $E_{\mathrm{int}}(\psi_{\mathrm{ion}})$ (3.18) will be accurately given by pure electrostatics as

$$E_{\mathrm{int}}(\psi_{\mathrm{ion}}) = -(r_{\mathrm{E}} + 2.797)^{-1} + \mathbb{P}_{\mathrm{E}} - 0.747 \tag{A 3.1}$$

where $\mathbb{P}_{\mathrm{E}}$ is the ionization potential of the element E, and 0.747 and 2.797 are the electron affinity of a hydrogen atom and the radius of an H^- ion. For E113 and E115 respectively the ionic radii are predicted to be 2.81 a.u. and 3.21 a.u. (paper III), while the most reliable estimates (paper III) of the first ionization potentials based on Dirac–Fock calculations (Paper I) are 7.9 eV and 5.5 eV. Substitution of these results in (A 3.1) predicts that $E_{\mathrm{int}}(\psi_{\mathrm{ion}})$ is $+2.3$ eV and $+0.2$ eV in the two cases respectively. These results are scarcely changed if the Dirac–Fock predictions for $\mathbb{P}_{\mathrm{E}}$ and the electron affinity of the hydrogen atom are used in (A 3.1) rather than values that take account of electron correlation because the decrease by 0.8 eV of $\mathbb{P}_{\mathrm{E}}$ is almost exactly counterbalanced by a corresponding decrease of the electron affinity. These results suggest that the expansion of (3.25) according to (3.26) is valid because the covalent binding energy will almost certainly be greater in magnitude than -1.0 eV estimated for H^{or}_{12} in the next paragraph. It should be pointed out both that H^{or}_{22} will be greater than these values of $E_{\mathrm{int}}(\psi_{\mathrm{ion}})$ because the ionic function $\mathrm{E}^+\mathrm{H}^-$ is not orthogonal to the covalent function and that inclusion of the overlap repulsion neglected in (A 3.1) improves the accuracy of expansion (3.26).

The two quantities $|H^{\mathrm{or}}_{22} - E_{\mathrm{int}}|$ and H^{or}_{12} may also be compared for LiH by using the integrals reported by Hurley (1958). If only the 1s and 2s Slater functions of the lithium are considered, the interaction energies $E_{\mathrm{int}}(^1\Sigma)$, (3.12*a*), and $E_{\mathrm{int}}(\psi^{\mathrm{NR}}_{\mathrm{ion}})$ are predicted to be -1.9 eV and -0.67 eV respectively, the latter quantity being calculated from the ionization potential and electron affinity predicted by the Hurley wavefunction. The value -2.2 eV calculated for $E^{\mathrm{NR}}_{\mathrm{int}}(\mathrm{i} - {}^1\Sigma)$, (3.23*a*), compared with the overlap Δ_{12} of 0.608, shows that $E_{\mathrm{int}}(\psi^{\mathrm{NR}}_{\mathrm{ion}})$ and H^{or}_{12} are -0.19 eV and -1.0 eV respectively. This confirms at least for this system, which is not atypical, that (3.25) can be expanded according to (3.26).

APPENDIX 4. A COMMENT ON THE ORDERS OF p̄–H AND p–H BONDS PREDICTED BY MOLECULAR ORBITAL THEORY

The methods used in §3 (*c*ii) to deduce the orders of the p̄–H and p–H bonds require that the bonding characteristics of the orbitals (3.39) are known. It should be pointed out that the argument that the p̄–H and p–H bond orders are $1-\frac{1}{3}S^2_{\mathrm{M0}}$ and $1-\frac{1}{6}S^2_{\mathrm{M0}}$ because the fractions $\frac{1}{3}S^2_{\mathrm{M0}}$ and $\frac{1}{6}S^2_{\mathrm{M0}}$ of the density do not contribute to the bonding implicity makes assumptions about the bonding characteristics of the functions (3.39). In this Appendix it is shown that the only reasonable alternative approach that is readily apparent yields predictions that are not qualitatively dissimilar to those presented in §3 (*c*).

In the alternative approach the large components (3.37 *a*) of the bonding relativistic molecular orbitals are expressed in terms of the p_1 function on the heavy element and the two spatial orbitals

$$\sigma = S_\sigma \tfrac{1}{\sqrt{2}}\,(\mathrm{p}_0+\mathrm{s}_0), \tag{A 4.1 a}$$

$$\sigma^* = S_{\sigma^*} \tfrac{1}{\sqrt{2}}\,(\mathrm{p}_0-\mathrm{s}_0), \tag{A 4.1 b}$$

so that neglecting overlap (i.e. $S_{\mathrm{M0}} = S_\sigma = S_{\sigma^*} = 1$)

$$|\phi\tfrac{1}{2}\rangle_{\mathrm{L}} = \tfrac{1}{2}(1+\sqrt{a})\,|\sigma\alpha\rangle+\tfrac{1}{2}(\sqrt{a}-1)\,|\sigma^*\alpha\rangle\mp\tfrac{1}{\sqrt{2}}\,(1-a)^{\frac{1}{2}}|\mathrm{p}_1\beta\rangle \tag{A 4.2}$$

If the arguments used in §3 (*c*ii) are not accepted, then the only reasonable assumption that can be made is that (A 4.1 *a*) is a fully bonding orbital while (A 4.1 *b*) is a fully anti-bonding one. This approach then predicts from (A 4.2) that the bond order is $\sqrt{a}\,(=\frac{1}{4}[(1+\sqrt{a})^2-(\sqrt{a}-1)^2])$ because the p_1 orbital is non-bonding. Clearly the bond order is still predicted to be $\sqrt{a}$ if this is taken to be $\frac{2}{3}$ and $\frac{5}{6}$ in the p̄ and p cases respectively of the order predicted by expanding the functions (3.39) in the orbitals (A 4.1). Furthermore the bond order is also predicted to be $\sqrt{a}$ if this is calculated by comparing the coefficient multiplying the overlap charge density $\mathrm{p}_0(\boldsymbol{r})\,\mathrm{s}_0(\boldsymbol{r})$ in (3.37 *a*) with the same coefficient in the orbital (A 4.1). It was pointed out in §3 (*c*ii) that the validity of this approach can be questioned.

The approach used in this Appendix predicts the orders of p̄–H and p–H bonds to be $\frac{1}{\sqrt{3}}$ (= 0.577) and $\sqrt{\frac{2}{3}}$ (= 0.81) respectively. The p–H prediction does not differ significantly from that ($\frac{5}{6}$ = 0.833) presented in §3 while the p̄–H prediction is not qualitatively dissimilar from that ($\frac{2}{3}$ = 0.667) derived in §3. It should be pointed out that the approach used in this Appendix rests on the somewhat arbitrary assumption that (3.37 *a*) should be expanded in the orbitals (A 4.1), while the arguments used in §3 (*c*ii) are independent of any such assumption. Consequently the predictions made in §3 should be regarded as more trustworthy than those presented in this Appendix.

APPENDIX 5. DETERMINATION OF THE KAPPA VALENCE WAVEFUNCTION FOR AN H–p–H SYSTEM

In §4 (*a*) it has been argued that both the coefficients c_i determining the Kappa valence wavefunction (4.12) for an H–p–H system and the equilibrium bond angle can be determined by maximizing the bond overlap *F* (4.16) subject to the condition (4.15). This condition taken in conjunction with (4.13) shows that

$$\left.\begin{aligned} c_3 &= \pm\langle \mathrm{t}_1|\mathrm{s}_1-\tfrac{1}{2}\rangle/(\langle \mathrm{t}_1|\mathrm{s}_1\tfrac{1}{2}\rangle^2+\langle \mathrm{t}|\mathrm{s}_1-\tfrac{1}{2}\rangle^2)^{\frac{1}{2}},\\ c_4 &= \mp\langle \mathrm{t}_1|\mathrm{s}_1\tfrac{1}{2}\rangle/(\langle \mathrm{t}_1|\mathrm{s}_1\tfrac{1}{2}\rangle^2+\langle \mathrm{t}_1|\mathrm{s}_1-\tfrac{1}{2}\rangle^2)^{\frac{1}{2}}, \end{aligned}\right\} \tag{A 5.1}$$

whence

$$F = (\langle \mathrm{t}_1|\mathrm{s}_1\tfrac{1}{2}\rangle^2 + \langle \mathrm{t}_1|\mathrm{s}_1-\tfrac{1}{2}\rangle^2)^{\frac{1}{2}}. \tag{A 5.2}$$

From the relations

$$\left.\begin{aligned} \langle \chi_1|\mathrm{s}_1\tfrac{1}{2}\rangle &= -\langle \chi_2|\mathrm{s}_1-\tfrac{1}{2}\rangle, \\ \langle \chi_1|\mathrm{s}_1-\tfrac{1}{2}\rangle &= \langle \chi_2|\mathrm{s}_1\tfrac{1}{2}\rangle, \end{aligned}\right\} \tag{A 5.3}$$

which are proved by using identities such as

$$\langle \chi_2|\mathrm{s}_1-\tfrac{1}{2}\rangle = \langle \chi_2|\hat{\mathrm{H}}_{y,\mathrm{t}}^{-1}\hat{\mathrm{H}}_{y,\mathrm{t}}|\mathrm{s}_1-\tfrac{1}{2}\rangle$$

and envoking (2.30) and (4.1), it follows that

$$F = (\langle \chi_1|\mathrm{s}_1\tfrac{1}{2}\rangle^2 + \langle \chi_2|\mathrm{s}_1\tfrac{1}{2}\rangle^2)^{\frac{1}{2}}. \tag{A 5.4}$$

This result shows that, after imposition of the condition (4.15), the bond overlap F is independent of the coefficients c_1–c_4 although clearly it still depends strongly on the molecular geometry. It thus follows that these coefficients are not uniquely defined by just the two conditions (4.15) and (4.16). This non-uniqueness arises because the wavefunction (4.12) can be written

$$\begin{aligned} |\psi_{\kappa\mathrm{v}}\rangle = S\hat{\mathscr{A}}\{|\mathrm{core}\rangle \times \tfrac{1}{\sqrt{2}}[(c_1c_3-c_2c_4)\,(|\chi_1\rangle|\mathrm{s}_1\tfrac{1}{2}\rangle - |\chi_2\rangle|\mathrm{s}_1-\tfrac{1}{2}\rangle) \\ +(c_1c_4+c_2c_3)\,(|\chi_1\rangle|\mathrm{s}_1-\tfrac{1}{2}\rangle + |\chi_2\rangle|\mathrm{s}_1\tfrac{1}{2}\rangle)] \times \tfrac{1}{\sqrt{2}}[(c_1c_3-c_2c_4)\,(|\chi_3\rangle|\mathrm{s}_2\tfrac{1}{2}\rangle - |\chi_4\rangle|\mathrm{s}_2-\tfrac{1}{2}\rangle) \\ -(c_1c_4+c_2c_3)\,(|\chi_3\rangle|\mathrm{s}_2-\tfrac{1}{2}\rangle + |\chi_4\rangle|\mathrm{s}_2\tfrac{1}{2}\rangle)]\}. \end{aligned} \tag{A 5.5}$$

However, it follows from (A 5.1) and (A 5.2) that

$$\left.\begin{aligned} c_3 &= \pm(c_1\langle \chi_1|\mathrm{s}_1-\tfrac{1}{2}\rangle + c_2\langle \chi_2|\mathrm{s}_1-\tfrac{1}{2}\rangle)/F, \\ c_4 &= \mp(c_1\langle \chi_1|\mathrm{s}_1\tfrac{1}{2}\rangle + c_2\langle \chi_2|\mathrm{s}_1-\tfrac{1}{2}\rangle)/F, \end{aligned}\right\} \tag{A 5.6}$$

and hence that

$$\left.\begin{aligned} c_1c_3-c_2c_4 &= \pm\langle \chi_2|\mathrm{s}_1\tfrac{1}{2}\rangle/F, \\ c_1c_4+c_2c_3 &= \mp\langle \chi_1|\mathrm{s}_1\tfrac{1}{2}\rangle/F. \end{aligned}\right\} \tag{A 5.7}$$

This shows through (A 5.5) that the wavefunction is independent of the choice of any one of the coefficients c_1–c_4 provided condition (4.15) is satisfied. This degree of freedom is most conveniently exploited by imposing the further orthogonality condition

$$\langle \mathrm{t}_1|(c_3\mathrm{s}_2\tfrac{1}{2} - c_4\mathrm{s}_2-\tfrac{1}{2})\rangle = 0, \tag{A 5.8}$$

which ensures that the hybrid $|\mathrm{t}_1\rangle$ does not overlap with one of the hydrogen orbitals in the other bond. This condition, taken in conjunction with the normalization condition (4.13), yields a second expression for both c_3 and c_4.

$$\left.\begin{aligned} c_3 &= \langle \mathrm{t}_1|\mathrm{s}_2-\tfrac{1}{2}\rangle/(\langle \mathrm{t}_1|\mathrm{s}_2\tfrac{1}{2}\rangle^2 + \langle \mathrm{t}_1|\mathrm{s}_2-\tfrac{1}{2}\rangle^2)^{\frac{1}{2}} \\ &= \langle \mathrm{t}_1|\mathrm{s}_1-\tfrac{1}{2}\rangle/(\langle \chi_1|\mathrm{s}_2\tfrac{1}{2}\rangle^2 + \langle \chi_2|\mathrm{s}_2\tfrac{1}{2}\rangle^2)^{\frac{1}{2}}, \\ c_4 &= \langle \mathrm{t}_1|\mathrm{s}_2\tfrac{1}{2}\rangle/(\langle \mathrm{t}_1|\mathrm{s}_2\tfrac{1}{2}\rangle^2 + \langle \mathrm{t}_1|\mathrm{s}_2-\tfrac{1}{2}\rangle^2)^{\frac{1}{2}} \\ &= \langle \mathrm{t}_1|\mathrm{s}_2\tfrac{1}{2}\rangle/(\langle \chi_1|\mathrm{s}_2\tfrac{1}{2}\rangle^2 + \langle \chi_2|\mathrm{s}_2\tfrac{1}{2}\rangle^2)^{\frac{1}{2}}. \end{aligned}\right\} \tag{A 5.9}$$

The second step in these two expressions follows in the same way as (A 5.6) is obtained from (A 5.1), namely by using the relations

$$\left.\begin{aligned} \langle \chi_1|\mathrm{s}_2-\tfrac{1}{2}\rangle &= \langle \chi_2|\mathrm{s}_2\tfrac{1}{2}\rangle, \\ \langle \chi_1|\mathrm{s}_2\tfrac{1}{2}\rangle &= -\langle \chi_2|\mathrm{s}_2-\tfrac{1}{2}\rangle, \end{aligned}\right\} \tag{A 5.10}$$

which are derived in the same way as (A 5.3). An equation determining c_1 is obtained by equating the two expressions (A 5.1) and (A 5.9) for c_3.

$$\frac{c_1\langle\chi_1|s_1-\frac{1}{2}\rangle+c_2\langle\chi_2|s_1-\frac{1}{2}\rangle}{(\langle\chi_1|s_1\frac{1}{2}\rangle^2+\langle\chi_2|s_1\frac{1}{2}\rangle^2)^{\frac{1}{2}}}=\frac{c_1\langle\chi_1|s_2-\frac{1}{2}\rangle+c_2\langle\chi_2|s_2-\frac{1}{2}\rangle}{(\langle\chi_1|s_2\frac{1}{2}\rangle^2+\langle\chi_2|s_2\frac{1}{2}\rangle^2)^{\frac{1}{2}}}$$
$$=\frac{-c_1\langle\chi_3|s_1-\frac{1}{2}\rangle+c_2\langle\chi_4|s_1-\frac{1}{2}\rangle}{(\langle\chi_3|s_1\frac{1}{2}\rangle^2+\langle\chi_4|s_1\frac{1}{2}\rangle^2)^{\frac{1}{2}}}. \qquad \text{(A 5.11)}$$

The second of these relations is derived from the first by using results such as $\langle\chi_1|s_2-\frac{1}{2}\rangle = \langle\chi_1|\hat{H}_{z,t}^{-1}\hat{H}_{z,t}|s_2-\frac{1}{2}\rangle = -\langle\chi_3|s_1-\frac{1}{2}\rangle$ where (4.1) and (2.31) are envoked. These relations show that all the coefficients c_1–c_4 are uniquely determined by the molecular geometry because this defines the overlap integrals entering (A 5.11) which uniquely fixes c_1 and c_2 and hence, through (A 5.6), c_3 and c_4.

The bond angle is determined by maximizing the bond overlap F. The contributions of the small components to this overlap will be smaller than those of the large components by a factor of c^2 and can therefore be neglected as discussed in §3 (*a*). The relations (3.9) show that the large components of the hybrids (4.11) are

$$\left.\begin{aligned}
|\chi_1\rangle_L &= |(\tfrac{1}{\sqrt{3}}p_z+\tfrac{1}{2}p_x)\,\alpha\rangle-\tfrac{1}{\sqrt{12}}|p_x\beta\rangle-\tfrac{1}{\sqrt{12}}i|p_y\beta\rangle+\tfrac{1}{2}i|p_y\alpha\rangle,\\
|\chi_2\rangle_L &= -[|(\tfrac{1}{\sqrt{3}}p_z+\tfrac{1}{2}p_x)\,\beta\rangle+\tfrac{1}{\sqrt{12}}|p_x\alpha\rangle-\tfrac{1}{\sqrt{12}}i|p_y\alpha\rangle-\tfrac{1}{2}i|p_y\beta\rangle],\\
|\chi_3\rangle_L &= |(-\tfrac{1}{\sqrt{3}}p_z+\tfrac{1}{2}p_x)\,\alpha\rangle+\tfrac{1}{\sqrt{12}}|p_x\beta\rangle+\tfrac{1}{\sqrt{12}}i|p_y\beta\rangle+\tfrac{1}{2}i|p_y\alpha\rangle,\\
|\chi_4\rangle_L &= -[|(-\tfrac{1}{\sqrt{3}}p_z+\tfrac{1}{2}p_x)\,\beta\rangle-\tfrac{1}{\sqrt{12}}|p_x\alpha\rangle+\tfrac{1}{\sqrt{12}}i|p_y\alpha\rangle-\tfrac{1}{2}i|p_y\beta\rangle],
\end{aligned}\right\} \qquad \text{(A 5.12)}$$

where $p_z = p_0$, and p_x and p_y are spatial orbitals related to the $p_{\pm1}$ appearing in (3.9) through $p_{\pm1} = \mp\frac{1}{\sqrt{2}}(p_x+ip_y)$. If we define the purely spatial integrals

$$S_x = \langle p_x|s_1\rangle, \quad S_z = \langle p_z|s_1\rangle, \qquad \text{(A 5.13)}$$

which are both positive, the relations (A 5.12) show that F is given by

$$F = \tfrac{1}{\sqrt{3}}(S_z^2+S_x^2+\sqrt{3}S_xS_z)^{\frac{1}{2}}. \qquad \text{(A 5.14)}$$

If we assume that the equilibrium bond lengths considered as a function of bond angle are insensitive to small displacements of this angle about its equilibrium value, the overlaps S_x and S_z are simply proportional to sin α and cos α respectively (figure 1). For these values of the overlaps, F is predicted to be maximized at $\alpha = 45°$ so that the H_2–E–H_1 bond angle is predicted to be 90°. If we neglect the contributions of the small components to the overlaps entering the equation (A 5.11) determining c_1 and c_2 this can be written in terms of the overlaps S_x and S_z by invoking the large components (A 5.12). The result is

$$[(-\tfrac{1}{\sqrt{3}}S_z+\tfrac{1}{2}S_x)^2+\tfrac{1}{12}S_x^2]^{\frac{1}{2}}\,[c_1(-\tfrac{1}{\sqrt{12}}S_x)+c_2(-\tfrac{1}{\sqrt{3}}S_z-\tfrac{1}{2}S_x)]$$
$$= [(\tfrac{1}{\sqrt{3}}S_z+\tfrac{1}{2}S_x)^2+\tfrac{1}{12}S_x^2]^{\frac{1}{2}}\,[-c_1(\tfrac{1}{\sqrt{12}}S_x)+c_2(\tfrac{1}{\sqrt{3}}S_z-\tfrac{1}{2}S_x)]. \qquad \text{(A 5.15)}$$

Solution of this equation, subject to (4.13), at the predicted equilibrium bond angle of 90° for which $S_x = S_z$, yields $c_1 = \frac{\sqrt{3}}{2}$ and $c_2 = \frac{1}{2}$ and hence through (A 5.6) $c_3 = c_4 = \frac{1}{\sqrt{2}}$. The alternative solution of (A 5.15) and (A 5.6) namely $c_1 = -\frac{1}{2}$, $c_2 = \frac{\sqrt{3}}{2}$, $c_3 = -c_4 = \frac{1}{\sqrt{2}}$ yields the identical wavefunction in (4.12).

It has therefore been shown that the Kappa-valence method predicts the H–p–H system to be bent with a bond angle of 90° and that the bonding can be described by the four hybrid orbitals (4.18) of the divalent heavy element.

APPENDIX 6. EXAMINATION OF THE QUANTITIES R_1–R_5 ENTERING THE KAPPA VALENCE DESCRIPTION OF HALIDES

(a) *Calculation of* R_1 *and* R_2

The quantities R_1 and R_2 defined by (6.21), which enter the expression (6.29) for the interaction energy predicted by the wavefunction (6.7), become after substitution of the large components (3.9) and neglect of the small components

$$\left.\begin{aligned} R_1 &= -\tfrac{1}{5}(1-a)\,\langle \mathrm{p}_{x,\,\mathrm{H}}|\mathrm{p}_x\rangle\,(\langle \mathrm{p}_x|\mathrm{p}_{x,\,\mathrm{H}}\rangle\langle \mathrm{p}_{x,\,\mathrm{H}}|\hat{\mathrm{G}}'_{R_1}|\mathrm{p}_{x,\,\mathrm{H}}\rangle-\langle \mathrm{p}_x|\hat{\mathrm{G}}'_{R_1}|\mathrm{p}_{x,\,\mathrm{H}}\rangle),\\ R_2 &= -\tfrac{1}{5}a\langle \mathrm{p}_{0,\,\mathrm{H}}|\mathrm{p}_0\rangle\,(\langle \mathrm{p}_0|\mathrm{p}_{0,\,\mathrm{H}}\rangle\langle \mathrm{p}_{0,\,\mathrm{H}}|\hat{\mathrm{G}}'_{R_2}|\mathrm{p}_{0,\,\mathrm{H}}\rangle-\langle \mathrm{p}_0|\hat{\mathrm{G}}'_{R_2}|\mathrm{p}_{0,\,\mathrm{H}}\rangle),\end{aligned}\right\}\tag{A 6.1}$$

with

$$\left.\begin{aligned} \hat{\mathrm{G}}'_{R_1} &= 2\hat{\mathrm{J}}_{\mathrm{p}_{y,\,\mathrm{H}}}+\hat{\mathrm{J}}_{\mathrm{p}_{x\,\mathrm{H}}}-3\hat{\mathrm{J}}_{\mathrm{p}_{0,\,\mathrm{H}}}-\hat{\mathrm{K}}_{\mathrm{p}_{y,\,\mathrm{H}}}-\hat{\mathrm{K}}_{\mathrm{p}_{0,\,\mathrm{H}}},\\ \hat{\mathrm{G}}'_{R_2} &= 4\hat{\mathrm{J}}_{\mathrm{p}_{x,\,\mathrm{H}}}-2\hat{\mathrm{K}}_{\mathrm{p}_{x,\,\mathrm{H}}}-4\hat{\mathrm{J}}_{\mathrm{p}_{0,\,\mathrm{H}}},\end{aligned}\right\}\tag{A 6.2}$$

where $\mathrm{p}_{x,\,\mu}$ and $\mathrm{p}_{y,\,\mu}$ are purely spatial orbitals for atom μ having p_x or p_y symmetry. By introducing the standard relation

$$\langle \mathrm{p}_x\mathrm{p}_{x,\,\mathrm{H}}|r_{12}^{-1}|\mathrm{p}_{x,\,\mathrm{H}}\mathrm{p}_{x,\,\mathrm{H}}\rangle = \langle \mathrm{p}_x\mathrm{p}_{y,\,\mathrm{H}}|r_{12}^{-1}|\mathrm{p}_{x,\,\mathrm{H}}\mathrm{p}_{y,\,\mathrm{H}}\rangle+2\langle \mathrm{p}_x\mathrm{p}_{y,\,\mathrm{H}}|r_{12}^{-1}|\mathrm{p}_{y,\,\mathrm{H}}\mathrm{p}_{x,\,\mathrm{H}}\rangle,\tag{A 6.3}$$

the results (A 6.1) simplify to

$$\left.\begin{aligned} R_1 &= \tfrac{1}{5}(1-a)\,\langle \mathrm{p}_{x,\,\mathrm{H}}|\mathrm{p}_x\rangle\langle \mathrm{p}_x|3\hat{\mathrm{J}}_{\mathrm{p}_{x,\,\mathrm{H}}}-3\hat{\mathrm{J}}_{\mathrm{p}_{z,\,\mathrm{H}}}+\hat{\mathrm{K}}_{\mathrm{p}_{x,\,\mathrm{H}}}-\hat{\mathrm{K}}_{\mathrm{p}_{0,\,\mathrm{H}}}|\mathrm{p}_{x,\,\mathrm{H}}\rangle,\\ R_2 &= a\langle \mathrm{p}_{0,\,\mathrm{H}}|\mathrm{p}_0\rangle\,(2\langle \mathrm{p}_0|\mathrm{p}_{0,\,\mathrm{H}}\rangle\langle \mathrm{p}_{0,\,\mathrm{H}}|\hat{\mathrm{K}}_{\mathrm{p}_{x,\,\mathrm{H}}}|\mathrm{p}_{0,\,\mathrm{H}}\rangle-\tfrac{1}{5}\langle \mathrm{p}_0|\hat{\mathrm{G}}'_{R_2}|\mathrm{p}_{0,\,\mathrm{H}}\rangle).\end{aligned}\right\}\tag{A 6.4}$$

In the discussion of the magnitude of R_1 and R_2 it is useful to introduce a complete set of halogen orbitals of which $\mathrm{p}_{0,\,\mathrm{H}}$, $\mathrm{p}_{x,\,\mathrm{H}}$ and $\mathrm{p}_{y,\,\mathrm{H}}$ are members and to invoke (A 6.3) to express (A 6.4) as

$$\left.\begin{aligned} R_1 &= \tfrac{1}{5}(1-a)\,\langle \mathrm{p}_{x,\,\mathrm{H}}|\mathrm{p}_x\rangle\sum_{\mathrm{a_H}}\langle \mathrm{p}_x|\mathrm{a_H}\rangle\langle \mathrm{a_H}|3\hat{\mathrm{J}}_{\mathrm{p}_{x,\,\mathrm{H}}}-3\hat{\mathrm{J}}_{\mathrm{p}_{z,\,\mathrm{H}}}+\hat{\mathrm{K}}_{\mathrm{p}_{x,}}-{}_{\mathrm{H}}\hat{\mathrm{K}}_{\mathrm{p}_{0,\,\mathrm{H}}}|\mathrm{p}_{x,\,\mathrm{H}}\rangle,\\ R_2 &= -2a\langle \mathrm{p}_{0,\,\mathrm{H}}|\mathrm{p}_0\rangle\sum_{\mathrm{a_H}\neq\mathrm{p}_{0,\,\mathrm{H}}}\langle \mathrm{p}_0|\mathrm{a_H}\rangle\langle \mathrm{a_H}|\hat{\mathrm{K}}_{\mathrm{p}_{x,\,\mathrm{H}}}|\mathrm{p}_{0,\,\mathrm{H}}\rangle.\end{aligned}\right\}\tag{A 6.5}$$

It can be argued first that R_1 is small because it consists, (A 6.4), the factor $\tfrac{1}{5}(1-a)\,\langle \mathrm{p}_{x,\,\mathrm{H}}|\mathrm{p}_x\rangle$ which is itself not large being disregarded, of a difference between pairs of integrals such as $\langle \mathrm{p}_x\mathrm{p}_{x,\,\mathrm{H}}|\hat{g}|\mathrm{p}_{x,\,\mathrm{H}}\mathrm{p}_{x,\,\mathrm{H}}\rangle$ and $\langle \mathrm{p}_0\mathrm{p}_{x,\,\mathrm{H}}|\hat{g}|\mathrm{p}_{0,\,\mathrm{H}}\mathrm{p}_{x,\,\mathrm{H}}\rangle$ ($g = r_{12}^{-1}$) which can be expected to be similar. Secondly it can be argued from (A 6.5) that R_1 is small because the result (A 6.3) shows that all the terms for which $|\mathrm{a_H}\rangle$ is a p orbital vanish so that the leading contributions come from terms for which this is a f or an h orbital. For diffuse f and h orbitals the two coulomb integrals will tend to equality, and the exchange integrals will be small, while the overlap $\langle \mathrm{p}_x|\mathrm{a_H}\rangle$ will not be large for the less diffuse functions. It can be similarly argued that R_2 is small either because it consists, (A 6.4), of a difference between two terms of similar magnitude or because it consists, (A 6.5), of the products of two overlap integrals multiplied by an exchange integral. These arguments are corroborated by the values $R_1 = -0.09$ eV and $R_2 = -0.077$ eV computed by using the Alchemey integrals programme, with the p orbitals on both centres taken to be 2p Slater functions with exponent 2.0, and the internuclear separation to be 1.7328 a.u. This system can be expected to provide a good estimate of R_1 and R_2 because a 2p Slater function of exponent 2.0 will approximate a fluorine 2p orbital, 1.7328 being the equilibrium internuclear distance in this molecule. Hence terms R_1 and R_2 do not affect the qualitative features of the bonding.

(*b*) *Calculation of R_4*

The quantity R_4, (6.40), enters the interaction energy (6.39) predicted by the wavefunction (6.35) which describes the interaction between the *j–j* coupled ground state of a heavy element and a halogen adopting its optimal valence state. This quantity consists of a difference between two matrix elements of the potential $\hat{\mathrm{G}}_4-\frac{4}{5}\hat{V}^{(0)}_{\mathrm{VH}}$. Since the operator $\hat{V}^{(0)}_{\mathrm{VH}}$, (6.2), is invariant under a unitary transformation of the halogen orbitals it can be expressed as

$$\hat{V}^{(0)}_{\mathrm{VH}} = \hat{\mathrm{G}}_4+\hat{\mathrm{G}}_{\mathrm{bH}\frac{1}{2},\,\mathrm{bH}\frac{1}{2}}+\hat{\mathrm{G}}_{\mathrm{bH}-\frac{1}{2},\,\mathrm{bH}-\frac{1}{2}}. \qquad \text{(A 6.6)}$$

It is useful to define the ket $|\mathrm{R}\rangle$ by

$$|\mathrm{R}\rangle = (\hat{\mathrm{G}}_4-\tfrac{4}{5}\hat{V}^{(0)}_{\mathrm{VH}})\,|\mathrm{b_H}\tfrac{1}{2}\rangle = \tfrac{1}{5}(\hat{\mathrm{G}}_4-4\hat{\mathrm{G}}_{\mathrm{bH}-\frac{1}{2},\,\mathrm{bH}-\frac{1}{2}})\,(-t_\sigma|\pi_{1,\,\mathrm{H}}\tfrac{1}{2}\rangle+t_\pi|z_{\mathrm{H}}\tfrac{1}{2}\rangle), \qquad \text{(A 6.7)}$$

where $|\mathrm{b_H}\frac{1}{2}\rangle$ has been expressed as (6.32). By expressing $\hat{\mathrm{G}}_4$ in terms of the spatial halogen orbitals $\mathrm{p}_{1,\,\mathrm{H}}$, $\mathrm{p}_{0,\,\mathrm{H}}$ and $\mathrm{p}_{-1,\,\mathrm{H}}$, the large components of $|\mathrm{R}\rangle$ are found to be

$$\begin{aligned}|\mathrm{R}\rangle_{\mathrm{L}} = \tfrac{1}{5}\{&[(1+t_\pi^2)\hat{\mathrm{J}}_{\mathrm{p}_{1,\mathrm{H}}}+(1+t_\pi^2-4t_\sigma^2)\hat{\mathrm{J}}_{\mathrm{p}_{-1,\mathrm{H}}}+(2t_\sigma^2-4t_\pi^2)\hat{\mathrm{J}}_{\mathrm{p}_{0,\mathrm{H}}}]\,(-t_\sigma|\mathrm{p}_{1,\,\mathrm{H}}\,\beta\rangle+t_\pi(\mathrm{p}_{0,\,\mathrm{H}}\,\alpha\rangle)\\ &+t_\sigma t_\pi(\hat{\mathrm{J}}_{\mathrm{p}_{1,\mathrm{H}}}-\hat{\mathrm{J}}_{\mathrm{p}_{0,\mathrm{H}}})\,(t_\pi|\mathrm{p}_{1,\,\mathrm{H}}\,\beta\rangle+t_\sigma|\mathrm{p}_{0,\,\mathrm{H}}\,\alpha\rangle)-(t_\pi\hat{\mathrm{J}}_{\mathrm{p}_{1,\mathrm{H}}\mathrm{p}_{0,\mathrm{H}}}|\mathrm{p}_{1,\,\mathrm{H}}\,\alpha\rangle\\ &-t_\sigma\hat{\mathrm{J}}_{\mathrm{p}_{-1,\mathrm{H}}\mathrm{p}_{1,\mathrm{H}}}|\mathrm{p}_{-1,\,\mathrm{H}}\,\beta\rangle)-[(5t_\sigma t_\pi^2\hat{\mathrm{J}}_{\mathrm{p}_{-1,\mathrm{H}}\mathrm{p}_{0,\mathrm{H}}}-t_\sigma(t_\sigma^2-4t_\pi^2)\hat{\mathrm{J}}_{\mathrm{p}_{0,\mathrm{H}}\mathrm{p}_{1,\mathrm{H}}})\,|\mathrm{p}_{0,\,\mathrm{H}}\,\beta\rangle\\ &+(t_\pi(t_\pi^2-4t_\sigma^2)\,\hat{\mathrm{J}}_{\mathrm{p}_{-1,\mathrm{H}}\mathrm{p}_{0,\mathrm{H}}}-5t_\sigma^2t_\pi\hat{\mathrm{J}}_{\mathrm{p}_{0,\mathrm{H}}\mathrm{p}_{1,\mathrm{H}}})\,|\mathrm{p}_{-1,\,\mathrm{H}}\,\alpha\rangle]\},\end{aligned} \qquad \text{(A 6.8)}$$

where the quantities $\hat{\mathrm{J}}_{\mathrm{p}_{m,\mathrm{H}}\mathrm{p}_{m',\mathrm{H}}}$ are coulomb operators built from the one-component functions $\mathrm{p}_{m,\,\mathrm{H}}$ and $\mathrm{p}_{m',\,\mathrm{H}}$ so that the matrix elements between the spinless one-component functions $|d\rangle$ and $|e\rangle$ are

$$\langle d|\hat{\mathrm{J}}_{\mathrm{p}_{m,\mathrm{H}}\mathrm{p}_{m',\mathrm{H}}}|e\rangle = \langle d\mathrm{p}_{m,\,\mathrm{H}}|\hat{g}|e\mathrm{p}_{m',\,\mathrm{H}}\rangle. \qquad \text{(A 6.9)}$$

The overlap between $|\mathrm{R}\rangle_{\mathrm{L}}$ and the ket

$$|\mathrm{L}\rangle_{\mathrm{L}} = c_\sigma|\mathrm{p}_{0,\,\mu}\,\alpha\rangle+c_\pi|\mathrm{p}_{1,\,\mu}\,\beta\rangle \qquad \text{(A 6.10)}$$

is found from (A 6.8), since $t_\sigma^2+t_\pi^2 = 1$, to be

$$\begin{aligned}\langle\mathrm{L}|\mathrm{R}\rangle_{\mathrm{L}\mu} = \tfrac{1}{5}\{&c_\pi t_\sigma[(5t_\sigma^2-3)\,(\langle\mathrm{p}_{1,\,\mu}\mathrm{p}_{1,\,\mathrm{H}}|\hat{g}|\mathrm{p}_{1,\,\mathrm{H}}\mathrm{p}_{1,\,\mathrm{H}}\rangle-\langle\mathrm{p}_{1,\,\mu}\mathrm{p}_{0,\,\mathrm{H}}|\hat{g}|\mathrm{p}_{1,\,\mathrm{H}}\mathrm{p}_{0,\,\mathrm{H}}\rangle)\\ &+\langle\mathrm{p}_{1,\,\mu}\mathrm{p}_{-1,\,\mathrm{H}}|\hat{g}|\mathrm{p}_{-1,\,\mathrm{H}}\mathrm{p}_{1,\,\mathrm{H}}\rangle+(10t_\sigma^2-9)\,\langle\mathrm{p}_{1,\,\mu}\mathrm{p}_{0,\,\mathrm{H}}|\hat{g}|\mathrm{p}_{0,\,\mathrm{H}}\mathrm{p}_{1,\,\mathrm{H}}\rangle]\\ &+c_\sigma t_\pi[(5t_\sigma^2-4)\,(\langle\mathrm{p}_{0,\,\mu}\mathrm{p}_{0,\,\mathrm{H}}|\hat{g}|\mathrm{p}_{0,\,\mathrm{H}}\mathrm{p}_{0,\,\mathrm{H}}\rangle-\langle\mathrm{p}_{0,\,\mu}\mathrm{p}_{1,\,\mathrm{H}}|\hat{g}|\mathrm{p}_{0,\,\mathrm{H}}\mathrm{p}_{1,\,\mathrm{H}}\rangle)\\ &-(2-10t_\sigma^2)\,\langle\mathrm{p}_{0,\,\mu}\mathrm{p}_{1,\,\mathrm{H}}|\hat{g}|\mathrm{p}_{1,\,\mathrm{H}}\mathrm{p}_{0,\,\mathrm{H}}\rangle]\}.\end{aligned} \qquad \text{(A 6.11)}$$

When μ is the halogen, this result can be simplified to

$$\langle\mathrm{L}|\mathrm{R}\rangle_{\mathrm{LH}} = \tfrac{1}{5}\langle\mathrm{p}_{1,\,\mathrm{H}}\mathrm{p}_{0,\,\mathrm{H}}|\hat{g}|\mathrm{p}_{0,\,\mathrm{H}}\mathrm{p}_{1,\,\mathrm{H}}\rangle\,[c_\pi t_\sigma(7-20t_\pi^2)+c_\sigma t_\pi(12-30t_\pi^2)] \qquad \text{(A 6.12)}$$

by invoking the relations

$$\left.\begin{aligned}\langle\mathrm{p}_{0,\,\mu}\mathrm{p}_{0,\,\mu}|\hat{g}|\mathrm{p}_{0,\,\mu}\mathrm{p}_{0,\,\mu}\rangle &= \langle\mathrm{p}_{1,\,\mu}\mathrm{p}_{1,\,\mu}|\hat{g}|\mathrm{p}_{1,\,\mu}\mathrm{p}_{1,\,\mu}\rangle+\langle\mathrm{p}_{1,\,\mu}\mathrm{p}_{-1,\,\mu}|\hat{g}|\mathrm{p}_{-1,\,\mu}\mathrm{p}_{1,\,\mu}\rangle,\\ \langle\mathrm{p}_{1,\,\mu}\mathrm{p}_{-1,\,\mu}|\hat{g}|\mathrm{p}_{-1,\,\mu}\mathrm{p}_{0,\,\mu}\rangle &= 2\langle\mathrm{p}_{1,\,\mu}\mathrm{p}_{0,\,\mu}|\hat{g}|\mathrm{p}_{0,\,\mu}\mathrm{p}_{1,\,\mu}\rangle.\end{aligned}\right\} \qquad \text{(A 6.13)}$$

The results (A 6.11) and (A 6.12) are useful because they can be used to express the quantity R_4 as

$$R_4 = \langle\mathrm{b_H}\tfrac{1}{2}|\mathrm{v_H}\tfrac{1}{2}\rangle_{\mathrm{L}}\,(\langle\mathrm{L}|\mathrm{R}\rangle_{\mathrm{LE}}-\langle\mathrm{b_H}\tfrac{1}{2}|\mathrm{v}\tfrac{1}{2}\rangle_{\mathrm{L}}\,\langle\mathrm{L}|\mathrm{R}\rangle_{\mathrm{LH}}). \qquad \text{(A 6.14)}$$

It can be argued that R_4 is small because it involves a difference between two similar terms, the first of which, $\langle\mathrm{L}|\mathrm{R}\rangle_{\mathrm{LE}}$, (A 6.11), is also a difference of similar integrals while the second, (A 6.12), is an exchange integral. This is corroborated for both $\bar{\mathrm{p}}$–Hal and p–Hal bonds by computations on the model systems used in the last section to examine R_1 and R_2. It is found for the $\bar{\mathrm{p}}$ and p cases respectively, after t_σ and t_π have been calculated from (6.46), that R_4 is indeed small having the values -0.059 eV and -0.065 eV.

(c) *Calculation of* R_5

The quantity R_5 defined below by (A 6.15) enters the interaction energy (6.48) predicted by the covalent wavefunction (6.47) describing the formation of a π bond between a halogen and a heavy element having a single valence electron occupying a Dirac–Fock p orbital:

$$R_5 = \tfrac{1}{5}\langle \mathrm{p_H}\tfrac{3}{2}|\mathrm{p}\tfrac{3}{2}\rangle(\langle \mathrm{p}\tfrac{3}{2}|\hat{\mathrm{G}}_{R_5}|\mathrm{p_H}\tfrac{3}{2}\rangle - \langle \mathrm{p}\tfrac{3}{2}|\mathrm{p_H}\tfrac{3}{2}\rangle\langle \mathrm{p_H}\tfrac{3}{2}|\hat{\mathrm{G}}_{R_5}|\mathrm{p_H}\tfrac{3}{2}\rangle), \tag{A 6.15}$$

where

$$\hat{\mathrm{G}}_{R_5} = \hat{\mathrm{G}}_{\pi_1,\mathrm{H}\frac{1}{2},\pi_1,\mathrm{H}\frac{1}{2}} + \hat{\mathrm{G}}_{\pi_{-1},\mathrm{H}-\frac{1}{2},\pi_{-1},\mathrm{H}-\frac{1}{2}} + \hat{\mathrm{G}}_{z\mathrm{H}\frac{1}{2},z\mathrm{H}\frac{1}{2}} + \hat{\mathrm{G}}_{z\mathrm{H}-\frac{1}{2},z\mathrm{H}-\frac{1}{2}} - 4\hat{\mathrm{G}}_{\mathrm{p}-\frac{3}{2},\mathrm{p}-\frac{3}{2}}, \tag{A 6.16}$$

The quantity R_5 becomes, when expressed in terms of solely the large components,

$$R_5 = \tfrac{1}{5}\langle \mathrm{p}_{x,\mathrm{H}}|\mathrm{p}_x\rangle(A - \langle \mathrm{p}_x|\mathrm{p}_{x,\mathrm{H}}\rangle B), \tag{A 6.17}$$

where

$$\left.\begin{aligned} A &= 2\langle \mathrm{p}_x\mathrm{p}_{0,\mathrm{H}}|\hat{g}|\mathrm{p}_{x,\mathrm{H}}\mathrm{p}_{0,\mathrm{H}}\rangle - \tfrac{3}{2}\langle \mathrm{p}_x\mathrm{p}_{x,\mathrm{H}}|\hat{g}|\mathrm{p}_{x,\mathrm{H}}\mathrm{p}_{x,\mathrm{H}}\rangle - \tfrac{1}{2}\langle \mathrm{p}_x\mathrm{p}_{y,\mathrm{H}}|\hat{g}|\mathrm{p}_{x,\mathrm{H}}\mathrm{p}_{y,\mathrm{H}}\rangle \\ &\qquad - \langle \mathrm{p}_x\mathrm{p}_{0,\mathrm{H}}|\hat{g}|\mathrm{p}_{0,\mathrm{H}}\mathrm{p}_{x,\mathrm{H}}\rangle - \langle \mathrm{p}_x\mathrm{p}_{y,\mathrm{H}}|\hat{g}|\mathrm{p}_{y,\mathrm{H}}\mathrm{p}_{x,\mathrm{H}}\rangle, \\ B &= \tfrac{3}{2}(\langle \mathrm{p}_{x,\mathrm{H}}\mathrm{p}_{y,\mathrm{H}}|\hat{g}|\mathrm{p}_{x,\mathrm{H}}\mathrm{p}_{y,\mathrm{H}}\rangle - \langle \mathrm{p}_{x,\mathrm{H}}\mathrm{p}_{x,\mathrm{H}}|\hat{g}|\mathrm{p}_{x,\mathrm{H}}\mathrm{p}_{x,\mathrm{H}}\rangle) \\ &\qquad - 2\langle \mathrm{p}_{x,\mathrm{H}}\mathrm{p}_{y,\mathrm{H}}|\hat{g}|\mathrm{p}_{y,\mathrm{H}}\mathrm{p}_{x,\mathrm{H}}\rangle. \end{aligned}\right\} \tag{A 6.18}$$

Considerations similar to those used to discuss the magnitudes of R_1 and R_2 indicate that R_5 will be small. This is corroborated by the value of 0.084 eV computed for the model problem used to investigate R_1 and R_2.

Appendix 7. Evaluation of a Fock matrix element entering the relativistic molecular orbital description of monohalides

It was shown in § 6 (*b*) that the vanishing of the Fock matrix element $\langle z_\mathrm{H}\tfrac{1}{2}|\hat{\mathrm{F}}_\mathrm{M}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle$ was the key feature which ensured that one of the molecular orbitals having $m_j = \tfrac{1}{2}$ was non-bonding, being located entirely on the halogen, and hence that the two remaining molecular orbitals having $m_j = \tfrac{1}{2}$ were respectively bonding and anti-bonding. This observation is merely a special case of the more general result that there will be one bonding, one anti-bonding and one halogen non-bonding orbital of $m_j = \tfrac{1}{2}$ if the Fock matrix element $\langle \chi_2\tfrac{1}{2}|\hat{\mathrm{F}}_\mathrm{M}|\chi_3\tfrac{1}{2}\rangle$ vanishes, where $|\chi_2\rangle$ and $|\chi_3\rangle$ are orthogonal halogen valence orbitals defined through

$$\left.\begin{aligned} |\chi_2 \pm \tfrac{1}{2}\rangle &= d_1|z_\mathrm{H} \pm \tfrac{1}{2}\rangle + d_2|\pi_{\pm 1,\mathrm{H}} \pm \tfrac{1}{2}\rangle, \\ |\chi_3 \pm \tfrac{1}{2}\rangle &= -d_2|z_\mathrm{H} \pm \tfrac{1}{2}\rangle + d_1|\pi_{\pm 1,\mathrm{H}} \pm \tfrac{1}{2}\rangle. \end{aligned}\right\} \tag{A 7.1}$$

The results of the calculation presented in § 6 (*b*) predicted that the valence molecular orbitals having $m_j = \pm\tfrac{1}{2}$ were

$$\left.\begin{aligned} |\phi_1\tfrac{1}{2}\rangle &= S_1(e_1|\mathrm{v}\tfrac{1}{2}\rangle + e_2|\chi_2\tfrac{1}{2}\rangle), \\ |\phi_2\tfrac{1}{2}\rangle &= |\chi_3\tfrac{1}{2}\rangle, \\ |\phi_1 - \tfrac{1}{2}\rangle &= S_1(e_1|\mathrm{v} - \tfrac{1}{2}\rangle + e_2|\chi_2 - \tfrac{1}{2}\rangle), \\ |\phi_2 - \tfrac{1}{2}\rangle &= |\chi_3 - \tfrac{1}{2}\rangle, \end{aligned}\right\} \tag{A 7.2}$$

with the coefficients d_1 and d_2 given by $-c_{22}$ and c_{32}, (6.63). Hence it is only necessary to show that $\langle\chi_2\tfrac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|\chi_3\tfrac{1}{2}\rangle$ vanishes to establish that the molecular orbitals (6.63) are indeed correct. The Dirac–Fock equations satisfied by the halogen valence orbitals show that the matrix element $\langle\chi_2\tfrac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|\chi_3\tfrac{1}{2}\rangle$ (F_{23}) reduces to $\langle\chi_2\tfrac{1}{2}|\hat{V}_{\mathrm{NE}}+\hat{V}_{\mathrm{DFE}}+\hat{V}_{\mathrm{val}}|\chi_3\tfrac{1}{2}\rangle$ which can, excepting the local part of the core potential $\hat{V}_{\mathrm{DFE}}$, be calculated by retaining solely the large components. If $|\phi\rangle$ is a molecular orbital whose large components have the form

$$|\phi\rangle_{\mathrm{L}} = c_1|\mathrm{A}\alpha\rangle+c_2|\mathrm{B}\beta\rangle, \tag{A 7.3}$$

the direct calculation using the large components (6.6) shows the matrix element $\langle\chi_2\tfrac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|\chi_3\tfrac{1}{2}\rangle$ to be given by

$$\begin{aligned}\langle\chi_2\tfrac{1}{2}|\hat{\mathrm{G}}_{\varphi,\varphi}|\chi_3\tfrac{1}{2}\rangle = {} & c_1^2 d_1 d_2(-\langle \mathrm{p}_{0,\mathrm{H}}\mathrm{A}|\hat{g}|\mathrm{p}_{0,\mathrm{H}}\mathrm{A}\rangle+\langle \mathrm{p}_{1,\mathrm{H}}\mathrm{A}|\hat{g}|\mathrm{p}_{1,\mathrm{H}}\mathrm{A}\rangle+\langle \mathrm{p}_{0,\mathrm{H}}\mathrm{A}|\hat{g}|\mathrm{A}\mathrm{p}_{0,\mathrm{H}}\rangle)\\ & +c_2^2 d_1 d_2(-\langle \mathrm{p}_{0,\mathrm{H}}\mathrm{B}|\hat{g}|\mathrm{p}_{0,\mathrm{H}}\mathrm{B}\rangle+\langle \mathrm{p}_{1,\mathrm{H}}\mathrm{B}|\hat{g}|\mathrm{p}_{1,\mathrm{H}}\mathrm{B}\rangle-\langle \mathrm{p}_{1,\mathrm{H}}\mathrm{B}|\hat{g}|\mathrm{B}\mathrm{p}_{1,\mathrm{H}}\rangle)\\ & +c_1 c_2(d_2^2\langle \mathrm{p}_{1,\mathrm{H}}\mathrm{A}|\hat{g}|\mathrm{B}\mathrm{p}_{0,\mathrm{H}}\rangle-d_1^2\langle \mathrm{p}_{0,\mathrm{H}}\mathrm{B}|\hat{g}|\mathrm{A}\mathrm{p}_{1,\mathrm{H}}\rangle).\end{aligned} \tag{A 7.4}$$

The contribution, denoted $F_{23\mathrm{v}}$, to F_{23} arising solely from the valence molecular orbitals is the sum of the six terms of the type (A 7.4):

$$F_{23\mathrm{v}} = \sum_{i=1}^{6}\langle\chi_2\tfrac{1}{2}|\hat{\mathrm{G}}_{\varphi_i,\varphi_i}|\chi_3\tfrac{1}{2}\rangle \equiv \sum_{i=1}^{6} F_{23\mathrm{v}}(\phi_i). \tag{A 7.5}$$

The six terms $F_{23\mathrm{v}}(\phi_i)$ are found by using (A 7.1)–(A 7.4) and (A 6.3) to be

$$F_{23\mathrm{v}}(\chi_3\tfrac{1}{2}) = 0, \tag{A 7.6a}$$

$$F_{23\mathrm{v}}(\chi_3-\tfrac{1}{2}) = [2d_1^3 d_2-3d_1 d_2^3-d_1 d_2(d_2^2-d_1^2)]\langle \mathrm{p}_{0,\mathrm{H}}\mathrm{p}_{x,\mathrm{H}}|\hat{g}|\mathrm{p}_{x,\mathrm{H}}\mathrm{p}_{0,\mathrm{H}}\rangle, \tag{A 7.6b}$$

$$F_{23\mathrm{v}}(\mathrm{p}\tfrac{3}{2}) = 2d_1 d_2\langle \mathrm{p}_{0,\mathrm{H}}\mathrm{p}_{x,\mathrm{H}}|\hat{g}|\mathrm{p}_{x,\mathrm{H}}\mathrm{p}_{0,\mathrm{H}}\rangle, \tag{A 7.6c}$$

$$F_{23\mathrm{v}}(\mathrm{p}-\tfrac{3}{2}) = 0 \tag{A 7.6d}$$

$$\begin{aligned}F_{23\mathrm{v}}(\phi_1\tfrac{1}{2}) = {} & d_1 d_2[-\langle \mathrm{p}_{0,\mathrm{H}}(e_2 d_1 \mathrm{p}_{0,\mathrm{H}}\mp\sqrt{a}\, e_1 \mathrm{p}_0)|\hat{g}|\mathrm{p}_{0,\mathrm{H}}(e_2 d_1 \mathrm{p}_{0,\mathrm{H}}\mp\sqrt{a}\, e_1 \mathrm{p}_0)\rangle\\ & +\langle \mathrm{p}_{1,\mathrm{H}}(e_2 d_1 \mathrm{p}_{0,\mathrm{H}}\mp\sqrt{a}\, e_1 \mathrm{p}_0)|\hat{g}|\mathrm{p}_{1,\mathrm{H}}(e_2 d_1 \mathrm{p}_{0,\mathrm{H}}\mp\sqrt{a}\, e_1 \mathrm{p}_0)\rangle\\ & +\langle \mathrm{p}_{0,\mathrm{H}}(e_2 d_1 \mathrm{p}_{0,\mathrm{H}}\mp\sqrt{a}\, e_1 \mathrm{p}_0)|\hat{g}|(e_2 d_1 \mathrm{p}_{0,\mathrm{H}}\mp\sqrt{a}\, e_1 \mathrm{p}_0)\mathrm{p}_{0,\mathrm{H}}\rangle\\ & -\langle \mathrm{p}_{0,\mathrm{H}}(e_2 d_2 \mathrm{p}_{1,\mathrm{H}}+e_1(1-a)^{\frac{1}{2}}\mathrm{p}_1)|\hat{g}|\mathrm{p}_{0,\mathrm{H}}(e_2 d_2 \mathrm{p}_{1,\mathrm{H}}+e_1(1-a)^{\frac{1}{2}}\mathrm{p}_1)\rangle\\ & +\langle \mathrm{p}_{1,\mathrm{H}}(e_2 d_2 \mathrm{p}_{1,\mathrm{H}}+e_1(1-a)^{\frac{1}{2}}\mathrm{p}_1)|\hat{g}|\mathrm{p}_{1,\mathrm{H}}(e_2 d_2 \mathrm{p}_{1,\mathrm{H}}+e_1(1-a)^{\frac{1}{2}}\mathrm{p}_1)\rangle\\ & -\langle \mathrm{p}_{1,\mathrm{H}}(e_2 d_2 \mathrm{p}_{1,\mathrm{H}}+e_1(1-a)^{\frac{1}{2}}\mathrm{p}_1)|\hat{g}|(e_2 d_2 \mathrm{p}_{1,\mathrm{H}}+e_1(1-a)^{\frac{1}{2}}\mathrm{p}_1)\mathrm{p}_{1,\mathrm{H}}\rangle]\\ & +d_2^2\langle \mathrm{p}_{1,\mathrm{H}}(e_2 d_1 \mathrm{p}_{0,\mathrm{H}}\mp\sqrt{a}\,\mathrm{p}_0)|\hat{g}|(e_2 d_2 \mathrm{p}_{1,\mathrm{H}}+e_1(1-a)^{\frac{1}{2}}\mathrm{p}_1)\mathrm{p}_{0,\mathrm{H}}\rangle\\ & -d_1^2\langle \mathrm{p}_{0,\mathrm{H}}(e_2 d_2 \mathrm{p}_{1,\mathrm{H}}+e_1(1-a)^{\frac{1}{2}}\mathrm{p}_1)|\hat{g}|(e_2 d_1 \mathrm{p}_{0,\mathrm{H}}\mp\sqrt{a}\, e_1 \mathrm{p}_0)\mathrm{p}_{1,\mathrm{H}}\rangle,\end{aligned} \tag{A 7.6e}$$

$$\begin{aligned}F_{23\mathrm{v}}(\phi_1-\tfrac{1}{2}) = {} & d_1 d_2[-\langle \mathrm{p}_{0,\mathrm{H}}(-e_2 d_2 \mathrm{p}_{-1,\mathrm{H}}\mp e_1(1-a)^{\frac{1}{2}}\mathrm{p}_{-1})|\hat{g}|\mathrm{p}_{0,\mathrm{H}}(-e_2 d_2 \mathrm{p}_{-1,\mathrm{H}}\mp e_1(1-a)^{\frac{1}{2}}\mathrm{p}_{-1})\rangle\\ & +\langle \mathrm{p}_{1,\mathrm{H}}(-e_2 d_2 \mathrm{p}_{-1,\mathrm{H}}\mp e_1(1-a)^{\frac{1}{2}}\mathrm{p}_{-1})|\hat{g}|\mathrm{p}_{1,\mathrm{H}}(-e_2 d_2 \mathrm{p}_{-1,\mathrm{H}}\mp e_1(1-a)^{\frac{1}{2}}\mathrm{p}_{-1})\rangle\\ & +\langle \mathrm{p}_{0,\mathrm{H}}(-e_2 d_2 \mathrm{p}_{-1,\mathrm{H}}\mp e_1(1-a)^{\frac{1}{2}}\mathrm{p}_{-1})|\hat{g}|(-e_2 d_2 \mathrm{p}_{-1,\mathrm{H}}\mp e_1(1-a)^{\frac{1}{2}}\mathrm{p}_{-1})\mathrm{p}_{0,\mathrm{H}}\rangle\\ & -\langle \mathrm{p}_{0,\mathrm{H}}(-e_2 d_1 \mathrm{p}_{0,\mathrm{H}}+e_1\sqrt{a}\,\mathrm{p}_0)|\hat{g}|\mathrm{p}_{0,\mathrm{H}}(-e_2 d_1 \mathrm{p}_{0,\mathrm{H}}+e_1\sqrt{a}\,\mathrm{p}_0)\rangle\\ & +\langle \mathrm{p}_{1,\mathrm{H}}(-e_2 d_1 \mathrm{p}_{0,\mathrm{H}}+e_1\sqrt{a}\,\mathrm{p}_0)|\hat{g}|\mathrm{p}_{1,\mathrm{H}}(-e_2 d_1 \mathrm{p}_{0,\mathrm{H}}+e_1\sqrt{a}\,\mathrm{p}_0)\rangle\\ & -\langle \mathrm{p}_{1,\mathrm{H}}(-e_2 d_1 \mathrm{p}_{0,\mathrm{H}}+e_1\sqrt{a}\,\mathrm{p}_0)|\hat{g}|(-e_2 d_1 \mathrm{p}_{0,\mathrm{H}}+e_1\sqrt{a}\,\mathrm{p}_0)\mathrm{p}_{1,\mathrm{H}}\rangle]\\ & +d_1^2\langle \mathrm{p}_{0,\mathrm{H}}(-e_2 d_1 \mathrm{p}_{0,\mathrm{H}}+e_1\sqrt{a}\,\mathrm{p}_0)|\hat{g}|(-e_2 d_2 \mathrm{p}_{-1,\mathrm{H}}\mp e_1(1-a)^{\frac{1}{2}}\mathrm{p}_{-1})\mathrm{p}_{1,\mathrm{H}}\rangle\\ & -d_2^2\langle \mathrm{p}_{1,\mathrm{H}}(-e_2 d_2 \mathrm{p}_{-1,\mathrm{H}}\mp e_1(1-a)^{\frac{1}{2}}\mathrm{p}_{-1})|\hat{g}|(-e_2 d_2 \mathrm{p}_{0,\mathrm{H}}+e_1\sqrt{a}\,\mathrm{p}_0)\mathrm{p}_{0,\mathrm{H}}\rangle.\end{aligned} \tag{A 7.6f}$$

The result (A 7.6*a*) taken in conjunction with the expression (A 7.2) for $|\phi_1 \tfrac{1}{2}\rangle$ shows that (A 7.6*e*) has no purely one-centre terms. The one-centre contributions, denoted $F_{23\mathrm{v1c}}(\phi_1 - \tfrac{1}{2})$ of (A 7.6*f*) are

$$F_{23\mathrm{v1c}}(\phi_1 - \tfrac{1}{2}) = d_1 d_2[3d_1^2 - 4d_2^2 + e_2^2(3d_2^2 - 4d_1^2)]\,\langle \mathrm{p}_{0,\mathrm{H}}\,\mathrm{p}_{x,\mathrm{H}}|\hat{g}|\mathrm{p}_{x,\mathrm{H}}\,\mathrm{p}_{0,\mathrm{H}}\rangle. \qquad \text{(A 7.7)}$$

The matrix element $F_{23\mathrm{v}}$ can be estimated by assuming both that halogen non-bonding orbital is determined by (6.61) and that the magnitudes of the overlaps $\langle \mathrm{p}_0|\mathrm{p}_{0,\mathrm{H}}\rangle$ and $\langle \mathrm{p}_1|\mathrm{p}_{1,\mathrm{H}}\rangle$ are equal. In this approximation $d_1 = \frac{1}{\sqrt{3}}$ and $d_2 = \sqrt{\frac{2}{3}}$ if $|\mathrm{v}\rangle$ is a $\bar{\mathrm{p}}$ orbital, while $d_1 = -\sqrt{\frac{2}{3}}$ and $d_2 = \frac{1}{\sqrt{3}}$ if $|\mathrm{v}\rangle$ is a p orbital. If one sets $e_1 = e_2 = \frac{1}{\sqrt{2}}$, the one-centre contribution ($F_{23\mathrm{v1c}}$) to $F_{23\mathrm{v}}$ is found to be

$$\left.\begin{aligned} F_{23\mathrm{v1c}} &= \tfrac{2\sqrt{2}}{9}\,\langle \mathrm{p}_{0,\mathrm{H}}\,\mathrm{p}_{x,\mathrm{H}}|\hat{g}|\mathrm{p}_{x,\mathrm{H}}\,\mathrm{p}_{0,\mathrm{H}}\rangle = -\tfrac{2\sqrt{2}}{75}\,F^{(2)}, \quad |\mathrm{v}\rangle = \bar{\mathrm{p}},\\ F_{23\mathrm{v1c}} &= -\tfrac{11\sqrt{2}}{18}\,\langle \mathrm{p}_{0,\mathrm{H}}\,\mathrm{p}_{x,\mathrm{H}}|\hat{g}|\mathrm{p}_{x,\mathrm{H}}\,\mathrm{p}_{0,\mathrm{H}}\rangle = -\tfrac{11\sqrt{2}}{150}\,F^{(2)}, \quad |\mathrm{v}\rangle = \mathrm{p}.\end{aligned}\right\} \qquad \text{(A 7.8)}$$

In the second step we have the relation

$$\langle \mathrm{p}_{0,\mathrm{H}}\,\mathrm{p}_{x,\mathrm{H}}|\hat{g}|\mathrm{p}_{x,\mathrm{H}}\,\mathrm{p}_{0,\mathrm{H}}\rangle = \tfrac{3}{25}F^{(2)}, \qquad \text{(A 7.9)}$$

where $F^{(2)}$ is the non-relativistic Slater integral for the halogen valence orbitals. The quantities (A 7.8) are found, by taking the value $F_2 = 0.25$ a.u. for chlorine (Pyper & Grant 1978), to be 0.26 eV and 0.70 eV in the $\bar{\mathrm{p}}$ and p cases respectively. Only (A 7.6*e*) and (A 7.6*f*) contain terms that are not purely one centre. These can be expected to be smaller than the former. Considering terms involving only one orbital of the heavy element, the third and sixth lines in square brackets in (A 7.6*e*) contain $\langle \mathrm{p}_{x,\mathrm{H}}\,\mathrm{p}_y|\hat{g}|\mathrm{p}_{y,\mathrm{H}}\,\mathrm{p}_{x,\mathrm{H}}\rangle$, which is the energy of interaction of two overlap charges densities whose nodal planes are mutually perpendicular, and is thus small. The remaining terms become, when expressed in terms of real orbitals,

$$\begin{aligned} 2d_1 d_2 e_1 e_2\{d_2\sqrt{\tfrac{2}{3}}[&-\langle \mathrm{p}_{0,\mathrm{H}}\,\mathrm{p}_x|\hat{g}|\mathrm{p}_{0,\mathrm{H}}\,\mathrm{p}_{x,\mathrm{H}}\rangle\\ &+\tfrac{1}{2}(\langle \mathrm{p}_{x,\mathrm{H}}\,\mathrm{p}_x|\hat{g}|\mathrm{p}_{x,\mathrm{H}}\,\mathrm{p}_{x,\mathrm{H}}\rangle + \langle \mathrm{p}_{x,\mathrm{H}}\,\mathrm{p}_y|\hat{g}|\mathrm{p}_{x,\mathrm{H}}\,\mathrm{p}_{y,\mathrm{H}}\rangle)]\\ &-d_1\tfrac{1}{\sqrt{3}}\,(-\langle \mathrm{p}_{0,\mathrm{H}}\,\mathrm{p}_0|\hat{g}|\mathrm{p}_{0,\mathrm{H}}\,\mathrm{p}_{0,\mathrm{H}}\rangle + \langle \mathrm{p}_{x,\mathrm{H}}\,\mathrm{p}_0|\hat{g}|\mathrm{p}_{x,\mathrm{H}}\,\mathrm{p}_{0,\mathrm{H}}\rangle)\}. \end{aligned} \qquad \text{(A 7.10)}$$

The term in (A 7.10) involving d_2 is the difference between the interaction of a π overlap charge density with one constructed from the halogen p_0 orbital and one constructed from a $\mathrm{p}_{-1,\mathrm{H}}$ orbital. Both this term and that involving d_1 can therefore be expected to be small. Test calculations for the model system used in Appendix 6 predict the d_2-term to be 0.07 eV and the d_1-term to be 0.13 eV. There are no terms in (A 7.6*f*) that involve just one orbital of the heavy element because such contributions in the pairs of lines (1 + 3), (5 + 6), (2 + 8) and (4 + 7) sum to zero. The terms in (A 7.6*c*) and (A 7.6*f*) containing an orbital of the heavy element twice sum to differences in two-centre coulomb integrals. Such differences will not be large and moreover are neglected when the diagonal Fock elements $\langle z_{\mathrm{H}}\,\tfrac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|z_{\mathrm{H}}\,\tfrac{1}{2}\rangle$ and $\langle \pi_{1,\mathrm{H}}\,\tfrac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|\pi_{1,\mathrm{H}}\,\tfrac{1}{2}\rangle$ are taken to be equal (§6(*b*)).

The only contribution to F_{23} not so far considered is that arising from the nucleus plus the core of the heavy element. The contribution of the local core potential becomes, with only the large components of the valence orbital retained, $d_1 d_2(\langle \mathrm{p}_{1,\mathrm{H}}|\hat{V}_{\mathrm{NE}} + \Sigma_{\mathrm{c}}\hat{\mathrm{J}}_{\mathrm{c}}|\mathrm{p}_{1,\mathrm{H}}\rangle - \langle \mathrm{p}_{0,\mathrm{H}}|\hat{V}_{\mathrm{NE}} + \Sigma_{\mathrm{c}}\hat{\mathrm{J}}_{\mathrm{c}}|\mathrm{p}_{0,\mathrm{H}}\rangle)$ which was neglected as small when the diagonal elements $\langle z_{\mathrm{H}}\,\tfrac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|z_{\mathrm{H}}\,\tfrac{1}{2}\rangle$ and

$\langle \pi_{1,\mathrm{H}}\tfrac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|\pi_{1,\mathrm{H}}\tfrac{1}{2}\rangle$ were taken to be equal. The contribution of the core exchange potentia can be written

$$-\langle \chi_2\tfrac{1}{2}|\sum_{\mathrm{c}}\hat{\mathrm{K}}_{\mathrm{c}}|\chi_3\tfrac{1}{2}\rangle = \sum_{\mathrm{c}} c_{1\mathrm{c}}c_{2\mathrm{c}}(d_2^2\langle \mathrm{p}_{1,\mathrm{H}}A_{\mathrm{c}}|\hat{g}|B_{\mathrm{c}}\mathrm{p}_{0,\mathrm{H}}\rangle - d_1^2\langle \mathrm{p}_{0,\mathrm{H}}B_{\mathrm{c}}|\hat{g}|A_{\mathrm{c}}\mathrm{p}_{1,\mathrm{H}}\rangle), \quad \text{(A 7.11)}$$

where $c_{1\mathrm{c}}$ and $c_{2\mathrm{c}}$ are the coefficients (A 7.3) of the purely spatial functions A_{c} and B_{c} associated with α and β spin respectively in the large components of core orbital $|\mathrm{c}\rangle$. The contributions in (A 7.11) arising both from core s orbitals and from core orbitals having $m_j = j$ vanish because either $c_{1\mathrm{c}}$ or $c_{2\mathrm{c}}$ is zero. For the remaining core orbitals the contributions from the core $\bar{1}$ and 1 orbitals have opposite signs and cancel exactly in the limit that the radial functions associated with the large components of such pairs of core orbitals are the same. Although these radial functions will not be identical for a heavy atom the individual exchange integrals are small and hence (A 7.11) can be neglected. It has therefore been shown that the matrix element $\langle \chi_2\tfrac{1}{2}|\hat{\mathrm{F}}_{\mathrm{M}}|\chi_3\tfrac{1}{2}\rangle$ is sufficiently small that its neglect does not invalidate the qualitative features of the bonding deduced in §6(*b*).

APPENDIX 8. MORE GENERAL CALCULATION OF MOLECULAR ORBITALS IN p² DIHALIDES

In this Appendix it is shown that for every bond angle there are still four non-bonding orbitals of $\hat{\mathrm{H}}_{z,\mathrm{t}}$-eigenvalue i located entirely on the halogens even if the resonance integrals (7.12) for pairs of orbitals aligned parallel and perpendicular to an E–Hal bond are not identical. It is further shown that the energies of the two bonding orbitals of $\hat{\mathrm{H}}_{z,\mathrm{t}}$-eigenvalue i are independent of the interbond angle if the two quantities (7.12) are equal.

After expressing the large components of both the orbitals $|\mathrm{p}\tfrac{3}{2}\rangle$ and $|\mathrm{p}-\tfrac{1}{2}\rangle$ and of the six functions (7.2) in terms of the functions $\mathrm{p}_{\parallel,\mu}$ and $\mathrm{p}_{\perp,\mu}$, the methods used to calculate the Fock matrix elements (7.6) show that the twelve matrix elements $\langle \chi_{\mathrm{H},i}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}m\rangle$ $(i = 1, 2, \ldots, 6)$ are given by

$$\left.\begin{array}{ll}
\langle \chi_{\mathrm{H},1}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}\tfrac{3}{2}\rangle = -(\cos^2\alpha F_{\perp} - \sin^2\alpha F_{\parallel}), & \langle \chi_{\mathrm{H},1}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}-\tfrac{1}{2}\rangle = \tfrac{1}{\sqrt{3}}(\cos^2\alpha F_{\perp} - \sin^2\alpha F_{\parallel}), \\
\langle \chi_{\mathrm{H},2}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}\tfrac{3}{2}\rangle = 0, & \langle \chi_{\mathrm{H},2}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}-\tfrac{1}{2}\rangle = \tfrac{2}{\sqrt{3}}(\sin^2\alpha F_{\perp} - \cos^2\alpha F_{\parallel}), \\
\langle \chi_{\mathrm{H},3}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}\tfrac{3}{2}\rangle = 0, & \langle \chi_{\mathrm{H},3}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}-\tfrac{1}{2}\rangle = 0, \\
\langle \chi_{\mathrm{H},4}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}\tfrac{3}{2}\rangle = 0, & \langle \chi_{\mathrm{H},4}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}-\tfrac{1}{2}\rangle = -\tfrac{2}{\sqrt{3}}\cos\alpha\sin\alpha(F_{\perp}+F_{\parallel}), \\
\langle \chi_{\mathrm{H},5}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}\tfrac{3}{2}\rangle = -\cos\alpha\sin\alpha(F_{\perp}+F_{\parallel}), & \langle \chi_{\mathrm{H},5}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}-\tfrac{1}{2}\rangle = \tfrac{1}{\sqrt{3}}\cos\alpha\sin\alpha(F_{\perp}+F_{\parallel}), \\
\langle \chi_{\mathrm{H},6}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}\tfrac{3}{2}\rangle = -iF_{\perp}, & \langle \chi_{\mathrm{H},6}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}-\tfrac{1}{2}\rangle = -\tfrac{1}{\sqrt{3}}iF_{\perp}.
\end{array}\right\} \quad \text{(A 8.1)}$$

All the remaining off-diagonal Fock matrix elements involving the eight having $\hat{\mathrm{H}}_{z,\mathrm{t}}$-eigenvalue i are zero. The results (A 8.1) show immediately that $|\chi_{\mathrm{H},3}\rangle$ is a non-bonding orbital located entirely on the halogens. The vanishing of both the matrix elements $\langle \chi_{\mathrm{H},2}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}\tfrac{3}{2}\rangle$ and $\langle \chi_{\mathrm{H},4}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}\tfrac{3}{2}\rangle$ shows that there is a linear combination of $|\chi_{\mathrm{H},2}\rangle$ and $|\chi_{\mathrm{H},4}\rangle$ which is a halogen non-bonding orbital. Furthermore, the equality of the ratios $\langle \chi_{\mathrm{H},5}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}\tfrac{3}{2}\rangle/\langle \chi_{\mathrm{H},5}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}-\tfrac{1}{2}\rangle$ and $\langle \chi_{\mathrm{H},1}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}\tfrac{3}{2}\rangle/\langle \chi_{\mathrm{H},1}|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}-\tfrac{1}{2}\rangle$ shows that a further non-bonding orbital can be constructed by taking linear combinations of $|\chi_{\mathrm{H},1}\rangle$ and $|\chi_{\mathrm{H},5}\rangle$. After defining the positive quantity

$$r = F_{\parallel}/F_{\perp} \quad \text{(A 8.2)}$$

the orbitals $|\chi_{\mathrm{H},1}\rangle$, $|\chi_{\mathrm{H},2}\rangle$, $|\chi_{\mathrm{H},4}\rangle$ and $|\chi_{\mathrm{H},5}\rangle$ are therefore replaced by the four orthogonal linear combinations

$$\left.\begin{aligned} |\mathrm{NBO}_1\rangle &= N_1[(\sin^2\alpha - r\cos^2\alpha)\,|\chi_{\mathrm{H},4}\rangle + \sin\alpha\cos\alpha(1+r)\,|\chi_{\mathrm{H},2}\rangle], \\ |\mathrm{NBO}_2\rangle &= N_2[(\cos^2\alpha - r\sin^2\alpha)\,|\chi_{\mathrm{H},5}\rangle - \sin\alpha\cos\alpha(1+r)\,|\chi_{\mathrm{H},1}\rangle], \\ |\chi_1\rangle &= N_1[\sin\alpha\cos\alpha(1+r)\,|\chi_{\mathrm{H},4}\rangle - (\sin^2\alpha - r\cos^2\alpha)\,|\chi_{\mathrm{H},2}\rangle], \\ |\chi_2\rangle &= N_2[\sin\alpha\cos\alpha(1+r)\,|\chi_{\mathrm{H},5}\rangle + (\cos^2\alpha - r\sin^2\alpha)\,|\chi_{\mathrm{H},1}\rangle], \end{aligned}\right\} \tag{A 8.3}$$

where N_1 and N_2 are normalization constants. Both the orbitals $|\mathrm{NBO}_1\rangle$ and $|\mathrm{NBO}_2\rangle$ have vanishing Fock matrix elements with both $|\mathrm{p}\tfrac{3}{2}\rangle$ and $|\mathrm{p}-\tfrac{1}{2}\rangle$ and are therefore non-bonding orbitals located entirely on the halogens. The four off-diagonal Fock matrix elements $\langle\chi_i|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}, m\rangle$ $(i = 1, 2)$ are found from (A 8.3) and (A 8.2) to be

$$\left.\begin{aligned} \langle\chi_1|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}\tfrac{3}{2}\rangle &= 0, \\ \langle\chi_1|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}-\tfrac{1}{2}\rangle &= N_1\,\tfrac{2}{\sqrt{3}}F_{\perp}[-\sin^2\alpha\cos^2\alpha(1+r)^2 - (\sin^2\alpha - r\cos^2\alpha)^2], \\ \langle\chi_2|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}\tfrac{3}{2}\rangle &= -N_2\,F_{\perp}[\sin^2\alpha\cos^2\alpha(1+r)^2 + (\cos^2\alpha - r\sin^2\alpha)^2], \\ \langle\chi_2|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}-\tfrac{1}{2}\rangle &= N_2\,\tfrac{1}{\sqrt{3}}F_{\perp}[\sin^2\alpha\cos^2\alpha(1+r)^2 + (\cos^2\alpha - r\sin^2\alpha)^2]. \end{aligned}\right\} \tag{A 8.4}$$

The two functions $|\chi_2\rangle$ and $|\chi_{\mathrm{H},6}\rangle$ are now replaced by two orthogonal linear combinations chosen such that one member $|\chi_2'\rangle$ does not interact with $|\mathrm{p}\tfrac{3}{2}\rangle$. This procedure is useful because it generates two functions $|\chi_1\rangle$ and $|\chi_2'\rangle$ which do not interact with $|\mathrm{p}\tfrac{3}{2}\rangle$ thereby enabling a non-bonding orbital interacting with neither $|\mathrm{p}\tfrac{3}{2}\rangle$ nor $|\mathrm{p}-\tfrac{1}{2}\rangle$ to be constructed as a linear combination of $|\chi_1\rangle$ and $|\chi_2'\rangle$. The two functions $|\chi_2'\rangle$ and $|\chi_3'\rangle$ defined by

$$\left.\begin{aligned} |\chi_2'\rangle &= N_3[\tfrac{1}{\sqrt{2}}|\chi_2\rangle + iN_2\,\tfrac{1}{\sqrt{2}}[\sin^2\alpha\cos^2\alpha(1+r)^2 + (\cos^2\alpha - r\sin^2\alpha)^2]\,|\chi_{\mathrm{H},6}\rangle, \\ |\chi_3'\rangle &= N_3[N_2\,\tfrac{1}{\sqrt{2}}[\sin^2\alpha\cos^2\alpha(1+r)^2 + (\cos^2\alpha - r\sin^2\alpha)^2]\,|\chi_2\rangle - \tfrac{1}{\sqrt{2}}i|\chi_{\mathrm{H},6}\rangle \end{aligned}\right\} \tag{A 8.5}$$

have Fock matrix elements that are calculated from (A 8.1) and (A 8.4) to be

$$\left.\begin{aligned} \langle\chi_2'|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}\tfrac{3}{2}\rangle &= 0, \\ \langle\chi_2'|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}-\tfrac{1}{2}\rangle &= N_2N_3\,\sqrt{\tfrac{2}{3}}\;F_{\perp}[\sin^2\alpha\cos^2\alpha(1+r)^2 + (\cos^2\alpha - r\sin^2\alpha)], \\ \langle\chi_3'|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}\tfrac{3}{2}\rangle &= -N_2N_3\,\tfrac{1}{\sqrt{2}}F_{\perp}\{[\sin^2\alpha\cos^2\alpha(1+r)^2 + (\cos^2\alpha - r\sin^2\alpha)^2]^2 + 1\}, \\ \langle\chi_3'|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}-\tfrac{1}{2}\rangle &= N_2N_3\,\tfrac{1}{\sqrt{6}}F_{\perp}\{[\sin^2\alpha\cos^2\alpha(1+r)^2 + (\cos^2\alpha - r\sin^2\alpha)^2]^2 - 1\}. \end{aligned}\right\} \tag{A 8.6}$$

The two functions $|\chi_1\rangle$ and $|\chi_2'\rangle$ are now replaced by the orthogonal linear combinations $|\mathrm{NBO}_3\rangle$ and $|\chi_2''\rangle$ defined as

$$\left.\begin{aligned} |\mathrm{NBO}_3\rangle &= N_4\{N_2N_3\,\tfrac{1}{\sqrt{3}}[\sin^2\alpha\cos^2\alpha(1+r)^2 + (\cos^2\alpha - r\sin^2\alpha)^2]\,|\chi_1\rangle \\ &\qquad + N_1\,\sqrt{\tfrac{2}{3}}[\sin^2\alpha\cos^2\alpha(1+r)^2 + (\sin^2\alpha - r\cos^2\alpha)^2]\,|\chi_2'\rangle\}, \\ |\chi_2''\rangle &= N_4\{N_1\,\sqrt{\tfrac{2}{3}}[\sin^2\alpha\cos^2\alpha(1+r)^2 + (\sin^2\alpha - r\cos^2\alpha)^2]\,|\chi_1\rangle \\ &\qquad - N_2N_3\,\tfrac{1}{\sqrt{3}}[\sin^2\alpha\cos^2\alpha(1+r)^2 + (\cos^2\alpha - r\sin^2\alpha)^2]\,|\chi_2'\rangle\}. \end{aligned}\right\} \tag{A 8.7}$$

In the steps (A 8.2)–(A 8.7) the six functions $|\chi_{\mathrm{H},1}\rangle$ to $|\chi_{\mathrm{H},6}\rangle$ (7.2) have been replaced by the functions $|\chi_{\mathrm{H},3}\rangle$, $|\mathrm{NBO}_1\rangle$, $|\mathrm{NBO}_2\rangle$, $|\mathrm{NBO}_3\rangle$, $|\chi_2''\rangle$ and $|\chi_3'\rangle$. The first four of these six functions have vanishing Fock matrix elements with both $|\mathrm{p}\tfrac{3}{2}\rangle$ and $|\mathrm{p}-\tfrac{1}{2}\rangle$ thus showing them to be non-bonding orbitals located entirely on the halogens. The four remaining molecular orbitals are obtained by diagonalizing the 4×4 matrix arising from the functions $|\mathrm{p}\tfrac{3}{2}\rangle$, $|\mathrm{p}-\tfrac{1}{2}\rangle$, $|\chi_2''\rangle$

and $|\chi_3'\rangle$. The only two off-diagonal Fock matrix elements not so far calculated are found from (A 8.7) and (A 8.6) to be

$$\left.\begin{aligned}\langle\chi_2''|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}\tfrac{3}{2}\rangle &= 0\\ \langle\chi_2''|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}-\tfrac{1}{2}\rangle &= -N_4\sqrt{2}\,F_{\perp}\{N_1^2\,\tfrac{2}{3}[\sin^2\alpha\cos^2\alpha(1+r)^2+(\sin^2\alpha-r\cos^2\alpha)^2]^2\\ &\quad+N_2^2N_3^2\,\tfrac{1}{3}[\sin^2\alpha\cos^2\alpha(1+r)^2+(\cos^2\alpha-r\sin^2\alpha)^2]^2\}.\end{aligned}\right\}\qquad(\mathrm{A}\ 8.8)$$

Solution of the 4 × 4 secular problem will yield two bonding and two anti-bonding orbitals.

The expressions for the molecular orbitals derived in the last paragraph greatly simplify if the resonance integrals $F_{\parallel}$ and $F_{\perp}$ (7.12) are equal. For this case the ratio r and hence all four normalization constants become unity. The four orbitals $|\chi_{\mathrm{H},3}\rangle$, $|\mathrm{NBO}_1\rangle$, $|\mathrm{NBO}_2\rangle$ and $|\mathrm{NBO}_3\rangle$ are still halogen non-bonding orbitals while $|\chi_2''\rangle$ and $|\chi_3'\rangle$ simplify to

$$\left.\begin{aligned}|\chi_2''\rangle &= \tfrac{1}{\sqrt{3}}(\sqrt{2}|\chi_1\rangle-|\chi_2'\rangle),\\ |\chi_3'\rangle &= \tfrac{1}{\sqrt{2}}(|\chi_2\rangle+i|\chi_{\mathrm{H},6}\rangle),\end{aligned}\right\}\qquad(\mathrm{A}\ 8.9)$$

with off-diagonal Fock matrix elements

$$\left.\begin{aligned}\langle\chi_2''|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}\tfrac{3}{2}\rangle &= 0, & \langle\chi_2''|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}-\tfrac{1}{2}\rangle &= -\sqrt{2}\,F_{\perp},\\ \langle\chi_3'|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}\tfrac{3}{2}\rangle &= -\sqrt{2}\,F_{\perp}, & \langle\chi_3'|\hat{\mathrm{F}}_{\mathrm{M}}|\mathrm{p}-\tfrac{1}{2}\rangle &= 0.\end{aligned}\right\}\qquad(\mathrm{A}\ 8.10)$$

These matrix elements immediately show that for all Hal–E–Hal bond angles there are two bonding molecular orbitals of energy $d+\sqrt{2}\,F_{\perp}$. This energy is identical to the energy of both the non-relativistic σ and π three-centre bonding orbitals.