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Phil. Trans. R. Soc. Lond. A 1986 **320**, 71-105
doi: 10.1098/rsta.1986.0105

Phil. Trans. R. Soc. Lond. A **320**, 71–105 (1986) [71]
Printed in Great Britain

RELATIVISTIC *AB INITIO* CALCULATIONS OF INTERACTION ENERGIES: FORMULATION AND APPLICATION TO IONIC SOLIDS

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(*Communicated by A. D. Buckingham, F.R.S. – Received* 3 *June* 1985)

CONTENTS

The theory and computational techniques used in a computer program capable of performing fully relativistic *ab initio* electronic structure calculations for pairs of interacting atomic species are presented. If the species are ions in a crystal, a description of an ionic solid is obtained. If the two species are otherwise free, the program yields a wavefunction for a diatomic molecule. The molecular wavefunction is an antisymmetrized product of core and valence parts. The core is a Hartree product of the Dirac–Fock atomic orbitals of the free atoms. The largest contribution to the energy arises from the inner-core orbitals, each having negligible overlap with all other orbitals. The purely atomic inner-core energy does not contribute to the binding energy of the molecule, thus obviating the need to calculate the largest part of the molecular energy. The outer core consists of those remaining closed subshells of the isolated atoms that are not significantly affected on molecule formation. All the remaining orbitals, including at least the valence Dirac–Fock atomic orbitals of the free atoms plus further atomic functions needed to describe charge density changes upon molecule formation, are used to construct the valence wavefunction. This can be constructed to take account of correlation between the valence electrons. All atomic functions have central field form with the radial parts defined numerically. This method of constructing the molecular wavefunction avoids the need for large basis sets, ensures that the Dirac small components bear the correct relation to the large components and avoids basis set superposition errors.

This program is used to initiate a non-empirical study of the properties of ionic solids. The results show that these properties cannot be reliably predicted by using free ion wavefunctions and that the Watson shell model for describing the non-negligible differences between free and in-crystal ion wavefunctions is not satisfactory. The results demonstrate the importance of inter-ionic dispersive attractions but show that it is not satisfactory to neglect the part quenching of the standard long-range form of these attractions arising from overlap of the ion wavefunctions.

1. INTRODUCTION

It is now well established that relativity significantly modifies the behaviour of even the valence electrons in a heavy element (Rose *et al.* 1978; Malli 1983). These modifications are introduced through two effects, called the direct and indirect relativistic effects (Mayers 1957; Rose *et al.* 1978). The indirect effect, absent from a one-electron atom, arises from the change in the electrostatic potential experienced by a valence electron because the charge distribution of the core electrons is modified by relativity. The direct relativistic effect, present even in a one-electron atom, originates from the change in the dynamics of the valence electron itself, arising because this is governed by the relativistic Dirac equation rather than by the non-relativistic Schrödinger equation. This effect is appreciable for s and $\bar{p}$ valence electrons (Grant 1970) in elements heavier than the third transition series. Furthermore, for such electrons this effect is too large for the relativistic correction to their energies to be accurately calculated by the first-order perturbation method (Pyper 1980*a*, 1981) of taking the expectation value over the non-relativistic orbitals of operators, such as the spin–orbit coupling, which describe relativistic corrections. This perturbation approach only yields the leading relativistic energy correction, which has order $1/c^2$ where c is the velocity of light in atomic units, and will therefore fail where relativistic effects are sufficiently large. Thus the first-order perturbation treatment recovers less than one half of the relativistic correction to the energy of the $6\bar{p}$ orbital in the thallium atom (Pyper & Marketos 1981), and predicts only one third of this correction for the 7s orbital in element 111 (Pyper 1983) where the non-relativistic eigenvalue of -0.201 a.u.† is decreased by relativity to -0.420 a.u. The perturbation approach is even unable to predict the expected negative sign of the substantial relativistic correction to the energy of the $7\bar{p}$ orbital in element 113 (Pyper 1983). Divergence difficulties prevent the

† 1 a.u. (atomic unit) = 1 hartree ≈ 4.359828 aJ.

perturbation method from being readily extended to higher order (Pyper 1980), although this is possible for the one-electron atom (Morrison & Moss 1980; Ketley & Moss 1983) which can be treated entirely analytically.

The importance of relativistic effects in heavy elements coupled with the failure of perturbation theory provide the motivation for developing calculations based directly on the Dirac equation. The first and main object of this paper is to present the formalism and describe the numerical methods used in the new computer program RIP (relativistic integrals program), capable of performing fully relativistic *ab initio* calculations for diatomic molecules. Very brief outlines of the formalism have been presented in preliminary studies by using RIP of both $(\mathrm{E}113)_2$ (Wood & Pyper 1981 *a*) and ionic solids containing superheavy elements (Wood & Pyper 1981 *b*), as well as in an investigation of the electron-gas method for calculating interatomic potentials (Wood & Pyper 1981 *c*). The molecular wavefunction is constructed from the Dirac–Fock atomic orbitals occupied in the constituent atoms augmented by further functions needed to describe the modification of the atomic charge densities concomitant on molecular formation. The second object of this paper is to describe the initial stage of a non-empirical study of ionic solids containing the heaviest ions, which has been made possible by the development of the RIP program. This stage reveals the inadequacies of present descriptions of both the dispersion energy and of the modifications of the ion wavefunctions induced by the crystalline environment. The refinements needed to rectify these two shortcomings to produce a trustworthy and physically sound description of ionic solids are described in the companion paper (Pyper 1986), which is concerned entirely with ionic solids.

2. The wavefunctions

(*a*) *Wavefunctions and hamiltonian*

The basic idea behind the RIP program is to express the wavefunction for the diatomic molecule in terms of the Dirac–Fock atomic orbitals of the constituent atoms. These atomic orbitals can be readily computed by using the Oxford Dirac–Fock program (Grant *et al.* 1980). This approach is useful because the innermost orbitals of heavy atoms, which contain most of the electrons, are scarcely affected by the formation of the molecule. This 'frozen core' approximation allows the wavefunction for the N-electron diatomic system to be written

$$|\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2 \ldots \boldsymbol{r}_N)\rangle = S\hat{\mathscr{A}}'[|\Phi_{1f}(\boldsymbol{r}_1 \ldots \boldsymbol{r}_{nf1})\rangle\, |\Phi_{2f}(\boldsymbol{r}_{nf1+1} \ldots \boldsymbol{r}_{nf1+nf2})\rangle \times |\Phi_v(\boldsymbol{r}_{nf1+nf2+1} \ldots \boldsymbol{r}_N)\rangle], \quad (2.1)$$

where S is a normalization constant and $\hat{\mathscr{A}}'$ is the partial antisymmetrizer that only interchanges coordinates between the sets $(\boldsymbol{r}_1 \ldots \boldsymbol{r}_{nf1})$, $(\boldsymbol{r}_{nf1+1} \ldots \boldsymbol{r}_{nf1+nf2})$ and $(\boldsymbol{r}_{nf1+nf2+1} \ldots \boldsymbol{r}_N)$. $|\Phi_{1f}(\boldsymbol{r}_1 \ldots \boldsymbol{r}_{nf1})\rangle$ and $|\Phi_{2f}(\boldsymbol{r}_{nf1+1} \ldots \boldsymbol{r}_{nf1+nf2})\rangle$ are wavefunctions containing $nf1$ and $nf2$ electrons respectively, for the cores of the atoms 1 and 2. These are taken to be single determinants of the core Dirac–Fock orbitals of the isolated atoms.

$$|\Phi_{1f}(\boldsymbol{r}_1 \ldots \boldsymbol{r}_{nf1})\rangle = \hat{\mathscr{A}}\left(\prod_{i=1}^{nf1} |u_{1,i}(\boldsymbol{r}_{1,i})\rangle\right), \quad (2.2a)$$

$$|\Phi_{2f}(\boldsymbol{r}_{nf1+1} \ldots \boldsymbol{r}_{nf1+nf2})\rangle = \hat{\mathscr{A}}\left(\prod_{i=1}^{nf2} |u_{2,i}(\boldsymbol{r}_{2,nf1+i})\rangle\right). \quad (2.2b)$$

Here $|u_{\mu,i}\rangle$ is the ith core orbital for atom μ, $\boldsymbol{r}_{\mu,i}$ is the position vector of electron i with respect to nucleus μ and $\hat{\mathscr{A}}$ is the antisymmetrizer. In (2.1) the quantity $|\boldsymbol{\Phi}_v(\boldsymbol{r}_{nf1+nf2+1}\ldots\boldsymbol{r}_N)\rangle$ is an antisymmetric molecular wavefunction for the valence electrons that is constructed from a set of relativistic orbitals not contained in either of the core functions (2.2). The number of electrons to be included in the valence function is determined by the accuracy required. Thus those electrons occupying open shells in the isolated atoms must be included, but the valence function can be enlarged to encompass those outermost core orbitals of the isolated atoms which are significantly affected by the formation of the molecule. The valence orbital set comprises both the outermost core orbitals and the occupied valence Dirac–Fock atomic orbitals of the isolated atoms, plus the further functions needed to describe the molecule.

Each of the orbitals used to construct the wavefunction (2.1) is taken to have the standard central field form (Grant 1970) with respect to the nucleus on which it is centred. They therefore carry the additional labels κ and m, taking the form

$$|u_{\mu,b}\,\kappa m\rangle = r_\mu^{-1}\begin{pmatrix} P_B(r_\mu)\,\chi_{\kappa,m}(\theta_\mu,\phi_\mu) \\ iQ_B(r_\mu)\,\chi_{-\kappa,m}(\theta_\mu,\phi_\mu)\end{pmatrix}, \tag{2.3}$$

where $P_B(r_\mu)$ and $Q_B(r_\mu)$ are radial functions centred on nucleus μ and $\chi_{\kappa,m}(\theta_\mu,\phi_\mu)$ is a vector-coupled space–spin function. These functions are eigenfunctions of the operators $\hat{j}^2$ and $\hat{j}_z$, corresponding to the total and z components of the angular momentum $(\hat{\boldsymbol{j}} = \hat{\boldsymbol{l}}+\hat{\boldsymbol{s}})$, with respective eigenvalues $j(j+1)$ and m so that m is the m_j quantum number.

$$\chi_{\kappa,m}(\theta_\mu,\phi_\mu) = \sum_{m_s=-\frac12}^{\frac12}\langle l\tfrac12(m-m_s)\,m_s\,|jm\rangle\,Y_{l,\,m-m_s}(\theta_\mu,\phi_\mu)\,|\tfrac12 m_s\rangle. \tag{2.4}$$

Here, $Y_{l,\,m-m_s}(\theta_\mu,\phi_\mu)$ is a spherical harmonic centred on nucleus μ and normalized such that $Y_{0,0} = 1/(2\pi^{\frac12})$, while $|\tfrac12 m_s\rangle$ is a two-component spin function

$$|\tfrac12\tfrac12\rangle = \begin{pmatrix}1\\0\end{pmatrix} \equiv |\alpha\rangle;\quad |\tfrac12-\tfrac12\rangle = \begin{pmatrix}0\\1\end{pmatrix} \equiv |\beta\rangle. \tag{2.5}$$

The quantum number κ defines both the total angular momentum j and the orbital angular momentum l through

$$\kappa = -(j+\tfrac12)\,a,\quad a = \begin{cases}+1 & \text{for}\quad j = l+\tfrac12 \\ -1 & \text{for}\quad j = l-\tfrac12.\end{cases} \tag{2.6}$$

The $(2j+1)$ orbitals, differing only in the m quantum number, are said to constitute a sub-shell (Grant *et al.* 1976) denoted by B, and are taken to have the same radial functions. The label b in (2.3) defines the orbital uniquely after specification of the centre μ, thus defining the κ and m_j quantum numbers which may both carry the additional subscript b. In the relativistic molecular orbital description of the valence function $|\boldsymbol{\Phi}_v(\boldsymbol{r}_{nf1+nf2+1}\ldots\boldsymbol{r}_N)\rangle$, the molecular orbitals are expressed as sums of central field orbitals (2.3) centred on both nuclei.

The orbitals given in (2.3) are constructed to maintain the appropriate relation between the large and small components (Grant 1982; Dyall *et al.* 1984) and thus lie within the sub-space of the electron-like solutions of some single-particle Dirac–Fock hamiltonian. The energy of the wavefunction (2.1) can therefore be evaluated as the expectation value of the relativistic hamiltonian $\mathscr{H}_{\mathrm{T}}$ (equation (2.7)), without the need to introduce any projection operators into an electron-like sub-space (Brown & Revenhall 1951; Mittleman 1972).

$$\hat{\mathscr{H}}_{\mathrm{T}} = \sum_{i=1}^{N} \hat{\mathscr{H}}_{\mathrm{D}}(i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} r_{ij}^{-1}; \tag{2.7}$$

$$\hat{\mathscr{H}}_{\mathrm{D}}(i) = \hat{\mathscr{H}}_{\mathrm{KE}}(i) + \hat{V}_{\mathrm{nuc}}(\boldsymbol{r}_i); \tag{2.8}$$

$$\hat{\mathscr{H}}_{\mathrm{KE}}(i) = c\boldsymbol{\alpha}(i)\cdot\hat{\boldsymbol{p}}(i) + c^2[\beta(i)-1]. \tag{2.9}$$

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, and $\hat{\boldsymbol{p}}(i)$ and $\hat{V}_{\mathrm{nuc}}(\boldsymbol{r}_i)$ respectively are operators for momentum and the potential energy of interaction with nuclei that are regarded as stationary point charges possessing no magnetic moments; c is the velocity of light. The quantities $\boldsymbol{\alpha}$ and β entering the kinetic energy (2.9) are 4×4 Dirac matrices

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma}^{\mathrm{P}} \\ \boldsymbol{\sigma}^{\mathrm{P}} & 0 \end{pmatrix} \quad \text{and} \quad \beta = \begin{pmatrix} \mathrm{I} & 0 \\ 0 & -\mathrm{I} \end{pmatrix}, \tag{2.10}$$

where $\boldsymbol{\sigma}^{\mathrm{P}}$ are the 2×2 Pauli matrices and I is a 2×2 identity matrix (Dirac 1958).

(b) *Atomic orbital symmetry*

The three operators $\hat{H}_{q,\,t}$, defined by

$$\hat{H}_{q,\,t} = i\Sigma_q \beta \hat{H}_{q,\,s}, \quad q = x, y, z, \tag{2.11}$$

with

$$\Sigma_q = \begin{pmatrix} \sigma_q^{\mathrm{P}} & 0 \\ 0 & \sigma_q^{\mathrm{P}} \end{pmatrix}, \tag{2.12}$$

are relativistic generalizations of those $\hat{H}_{x,\,s}$, $\hat{H}_{y,\,s}$ and $\hat{H}_{z,\,s}$ corresponding to spatial reflections in the yz, xz and xy planes (Pyper 1982). The time reversal operator $\hat{T}_{\mathrm{R}}$ is given by (Rose 1961)

$$\hat{T}_{\mathrm{R}} = i\Sigma_2 \hat{K}, \tag{2.13}$$

where $\hat{K}$ is the complex conjugation operator. In a coordinate system having an origin midway between the two nuclei, with the z aligned along the internuclear axis, the one-electron hamiltonian $\hat{\mathscr{H}}_{\mathrm{D}}$ for each electron commutes with $\hat{H}_{x,\,t}$, $\hat{H}_{y,\,t}$ (Pyper 1982) and $\hat{T}_{\mathrm{R}}$ (Rose 1961) and, in a homonuclear system, with $\hat{H}_{z,\,t}$ also (Pyper 1982):

$$\begin{aligned}[\hat{\mathscr{H}}_{\mathrm{D}}(i), \hat{H}_{q,\,t}(i)] &= [\hat{\mathscr{H}}_{\mathrm{D}}(i), \hat{T}_{\mathrm{R}}(i)] = [\{\hat{T}_{\mathrm{R}}(i)\ \hat{T}_{\mathrm{R}}(j)\}, r_{ij}^{-1}] \\ &= [\{\hat{H}_{q,\,t}(i)\ \hat{H}_{q,\,t}(j)\}, r_{ij}^{-1}] = 0. \end{aligned} \tag{2.14}$$

The orbitals (2.3) are transformed under (2.11) and (2.13) according to the following (Pyper 1982):

$$\hat{H}_{x,\,t}|u_{\mu,\,b}\,\kappa_b\,m\rangle = i(-1)^{\frac{1}{2}(1-a_b)}\,|u_{\mu,\,b}\,\kappa_b\,{-m}\rangle; \tag{2.15}$$

$$\hat{H}_{y,\,t}|u_{\mu,\,b}\,\kappa_b\,m\rangle = (-1)^{m+\frac{1}{2}}(-1)^{\frac{1}{2}(1-a_b)}\,|u_{\mu,\,b}\,\kappa_b\,{-m}\rangle; \tag{2.16}$$

$$\hat{H}_{z,\,t}|u_{\mu,\,b}\,\kappa_b\,m\rangle = i(-1)^{j_b-m+\frac{1}{2}(1-a_b)}\,|u_{\mu',\,b}\,\kappa_b\,m\rangle \quad (\mu' \neq \mu); \tag{2.17}$$

$$\hat{T}_{\mathrm{R}}|u_{\mu,\,b}\,\kappa_b\,m\rangle = \hat{H}_{y,\,t}|u_{\mu,\,b}\,\kappa_b\,m\rangle. \tag{2.18}$$

The result (2.17) applies only to a homonuclear system which is taken to have the same set orbitals, specified by the label b, on both centres. The result (2.18) is derived by the method used to obtain (2.16) (Pyper 1982).

Combining the result (2.16) with $\hat{H}^{+}_{y,\,t}(i)\,\hat{H}_{y,\,t}(i) = 1$ establishes the following (Pyper 1982):

$$\langle u_{\mu,\,b}\,\kappa_b\,m\,|u_{\mu',\,c}\,\kappa_c\,m\rangle = (-1)^{\frac{1}{2}(a_b-a_c)}\,\langle u_{\mu,\,b}\,\kappa_b-m|u_{\mu',\,c}\,\kappa_c-m\rangle; \tag{2.19a}$$

$$\langle u_{\mu,\,b}\,\kappa_b\,m|\hat{\mathscr{H}}_{\mathrm{KE}}|u_{\mu',\,c}\,\kappa_c\,m\rangle = (-1)^{\frac{1}{2}(a_b-a_c)}\,\langle u_{\mu,\,b}\,\kappa_b-m|\hat{\mathscr{H}}_{\mathrm{KE}}|u_{\mu',\,c}\,\kappa_c-m\rangle; \tag{2.19b}$$

$$\langle u_{\mu,\,b}\,\kappa_b\,m|\hat{V}_{\mathrm{nuc}}|u_{\mu',\,c}\,\kappa_b\,m\rangle = (-1)^{\frac{1}{2}(a_b-a_c)}\,\langle u_{\mu,\,b}\,\kappa_b-m|\hat{V}_{\mathrm{nuc}}|u_{\mu',\,c}\,\kappa_c-m\rangle; \tag{2.19c}$$

$$\begin{aligned}\langle u_{\mu,\,b}\,\kappa_b\,m_b\,u_{\mu',\,c}\,\kappa_c\,m_c|r_{12}^{-1}|u_{\mu'',\,d}\,\kappa_d\,m_d\,u_{\mu''',\,e}\,\kappa_e\,m_e\rangle &= (-1)^{\frac{1}{2}(a_b+a_c-a_d-a_e)}\\ &\quad\langle u_{\mu,\,b}\,\kappa_b-m_b\,u_{\mu',\,c}\,\kappa_c-m_c|r_{12}^{-1}|u_{\mu'',\,d}\,\kappa_d-m_d\,u_{\mu''',\,e}\,\kappa_e-m_e\rangle,\end{aligned} \tag{2.19d}$$

where $\langle\phi_b\,\phi_c|r_{12}^{-1}|\phi_d\,\phi_e\rangle$ is the relativistic electron–electron repulsion integral $\int\int\phi_b(\boldsymbol{r}_1)^{+}\,\phi_c(\boldsymbol{r}_2)^{+}\,r_{12}^{-1}\,\phi_d(\boldsymbol{r}_1)\,\phi_e(\boldsymbol{r}_2)\,\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2$, with $\phi_g(\boldsymbol{r}_2)$ a four-component Dirac orbital. The integrals (2.19d) vanish unless $m_b+m_c = m_d+m_e$. For a homonuclear system, use of the identity $\hat{H}^{+}_{z,\,t}\,\hat{H}_{z,\,t} = 1$ shows that

$$\langle u_{\mu,\,b}\,\kappa_b\,m\,|u_{\mu',\,c}\,\kappa_c\,m\rangle = (-1)^{j_c-j_b}\,(-1)^{\frac{1}{2}(a_b-a_c)}\,\langle u_{\mu',\,b}\,\kappa_b\,m\,|u_{\mu,\,c}\,\kappa_c\,m\rangle,\quad (\mu'\neq\mu). \tag{2.20}$$

3. CLOSED-SHELL SYSTEMS

(a) *Wavefunction construction*

The wavefunction describing the interaction of two closed-shell systems is a simplified form of (2.1):

$$|\Psi(\boldsymbol{r}_1\ldots\boldsymbol{r}_N)\rangle = S\mathscr{A}(|\Phi_1(\boldsymbol{r}_1\ldots\boldsymbol{r}_{n1})\rangle\,|\Phi_2(\boldsymbol{r}_{n1+1}\ldots\boldsymbol{r}_N)\rangle), \tag{3.1}$$

where $N = n1+n2$. It is now required to determine the expectation value of $\mathscr{H}_{\mathrm{T}}$(2.7) with this wavefunction. This is complicated because the orbitals used to construct the wavefunction (2.2a) for atom 1 are not orthogonal to those entering the wavefunction (2.2b) of atom 2. However, the wavefunction (3.1) is invariant to a linear transformation of the atomic orbitals, so that the calculation of $\langle\Psi|\mathscr{H}_{\mathrm{T}}|\Psi\rangle$ may be simplified by extracting an orthonormal set from the atomic orbitals of the two atoms. This is achieved by using Schmidt orthogonalization.

First an 'inner' core of orbitals is defined. These are a set of core orbitals taken from both atoms such that any pair of orbitals on different atoms have negligible overlap. In a homonuclear system the 'inner' core contains identical orbitals from each atom. The orbitals remaining after removal of the inner core are termed the 'outer' core. The outer-core orbitals are ordered in terms of increasing mean radius and a new orbital list is then defined, consisting of the inner-core orbitals of atom 1, followed by those of atom 2, followed by the ordered list of outer-core orbitals. Each set of atomic orbitals having a particular m value is treated as a separate group because orbitals of different m are already orthogonal. The ordered orbital list is:

$$|u_1\,\kappa_1\,m\rangle\ldots|u_{ncm}\,\kappa_{ncm}\,m\rangle, |u_{ncm+1}\,\kappa_{ncm+1}\,m\rangle,\ldots|u_{Nm}\,\kappa_{Nm}\,m\rangle, \tag{3.2}$$

where ncm is the total number of inner core orbitals with $m_j = m$, and Nm is the total number of inner- plus outer-core orbitals with $m_j = m$. It should be noted that the label i on atomic orbital $|u_i \, k_i \, m\rangle$ in (3.2) is a label in this new combined list; there is no label denoting the nuclear centre although for the inner-core orbitals one has

$$|u_i \, \kappa_i \, m\rangle = |u_{1,\,i} \, \kappa_i \, m\rangle; \quad i \leqslant nc1m, \tag{3.3a}$$

$$|u_i \, \kappa_i \, m\rangle = |u_{2,\;i-nc1m} \; k_{i-nc1m} \; m\rangle. \quad nc1m < i \leqslant ncm. \tag{3.3b}$$

Here, $nc\mu m$ is the total number of inner-core orbitals on atom μ having $m_j = m$ so that $nc1m+nc2m = ncm$. On the right side of (3.3), the first subscript containing i is a number defining the position in a list of orbitals on atom μ having $m_j = m$, and therefore differs from the more general label b in (2.3) which defines both the sub-shell and the m_j quantum number. Starting with the first outer-core orbital, each orbital is in turn orthogonalized to all of the orbitals appearing before it in the ordered list and then replaced in the list. The first 'molecular outer-core orbital' thus obtained is

$$|\phi_i \, m\rangle = S_i\Big(|u_i \, \kappa_i \, m\rangle - \sum_{j=1}^{ncm} \langle u_j \, \kappa_j \, m \,|u_i \, \kappa_i \, m\rangle \, |u_j \, \kappa_j \, m\rangle\Big), \tag{3.4}$$

where $i = ncm+1$ and S_i is a normalization constant. Subsequent molecular outer-core orbitals are given by

$$|\phi_i \, m\rangle = S_i(|u_i \, \kappa_i \, m\rangle - \sum_{j=1}^{ncm} \langle u_j \, \kappa_j \, m \,|u_i \, \kappa_i \, m\rangle \, |u_j \, \kappa_j \, m\rangle - \sum_{j=ncm+1}^{i-1} \langle \phi_j \, m \,|u_i \, \kappa_i \, m\rangle \, |\phi_j \, m\rangle). \tag{3.5}$$

Only the orbitals with positive m need to be explicitly constructed because it is shown in §3b that those having negative m can be related to those with positive m by using the operator $\hat{H}_{y,\,t}$.

A slightly different procedure is used for symmetric molecules. Here the atomic orbitals with a common value of m are ordered according to (3.2) and (3.3), but each pair of equivalent outer-core orbitals from centres 1 and 2 are kept together. The first stage in generating the first pair of orthonormal outer-core orbitals is to replace $|u_{1,\,i} \, k_i \, m\rangle$ and $|u_{2,\,i} \, k_i \, m\rangle$, where $i = \tfrac{1}{2}ncm+1$, by the two molecular outer-core orbitals $|\phi_{1,\,i} \, m\rangle$ and $|\phi_{2,\,i} \, m\rangle$ defined by

$$|\phi_{\mu,\,i} \, m\rangle = S_i(|u_{\mu,\,i} \, \kappa_i \, m\rangle - \sum_{j=1}^{\frac{1}{2}ncm} \langle u_{\mu',\,j} \, \kappa_j \, m \,|u_{\mu,\,i} \, \kappa_i \, m\rangle \, |u_{\mu',\,j} \, \kappa_j \, m\rangle), \quad (\mu' \neq \mu), \tag{3.6}$$

even though these two orbitals are not orthogonal to each other. The first stage in the construction of subsequent pairs of orthonormal outer-core orbitals is slightly more complex, because they must be orthogonalized to each orbital already present in previously generated pairs of molecular outer-core orbitals, as well as to the inner-core orbitals. Thus the atomic orbital $|u_{\mu,\,i} \, \kappa_i \, m\rangle$ is replaced by

$$\begin{aligned} |\phi_{\mu,\,i} \, m\rangle = S_i[|u_{\mu,\,i} \, \kappa_i \, m\rangle &- \sum_{j=1}^{\frac{1}{2}ncm} \langle u_{\mu',\,j} \, \kappa_j \, m \,|u_{\mu,\,i} \, \kappa_i \, m\rangle \, |u_{\mu',\,j} \, \kappa_j \, m\rangle \\ &- \sum_{j=(\frac{1}{2}ncm)+1}^{i-1} (\langle \phi_{\mu,\,j} \, m \,|u_{\mu,\,i} \, \kappa_i \, m\rangle \, |\phi_{\mu,\,j} \, m\rangle \\ &+ \langle \phi_{\mu',\,j} \, m \,|u_{\mu,\,i} \, \kappa_i \, m\rangle \, |\phi_{\mu',\,j} \, m\rangle)]. \end{aligned} \tag{3.7}$$

After the procedure (3.7) has been executed for each pair of outer-core orbitals $|u_{1,\,i} \, \kappa_i \, m\rangle$ and $|u_{2,\,i} \, \kappa_i \, m\rangle$, the two orbitals $|\phi_{1,\,i} \, m\rangle$ and $|\phi_{2,\,i} \, m\rangle$ constituting pair i are orthogonal both to the inner-core orbitals and to all molecular outer-core orbitals in all other pairs $i' \neq i$. However, for each pair of molecular outer-core orbitals i constructed according to (3.7), the orbitals

$|\phi_{1,i}\, m\rangle$ and $|\phi_{2,i}\, m\rangle$ are not orthogonal to each other. This is rectified by defining the pairs of orthonormal outer-core orbitals

$$|\phi_{i\pm}\, m\rangle = 2^{-\frac{1}{2}} S_i(|\phi_{1,i}\, m\rangle \pm |\phi_{2,i}\, m\rangle). \tag{3.8}$$

The orbital set composed of the inner core defined according to (3.3) plus the $(Nm - Ncm)$ orthonormal outer-core orbitals defined in (3.8) is fully orthonormal.

For both homonuclear and heteronuclear molecules, the wavefunction (3.1) is expressed in terms of the orthonormal set of orbitals as

$$|\Psi(\boldsymbol{r}_1, \dots \boldsymbol{r}_N)\rangle = \hat{\mathscr{A}}\left[\prod_m \left(\prod_{i=1}^{ncm} |u_i\, \kappa_i\, m\rangle\right)\left(\prod_{i=ncm+1}^{Nm} |\phi_i\, m\rangle\right)\right]. \tag{3.9}$$

Here the electron coordinates not written explicitly on the right side are defined by the convention that, in the identity permutation in the antisymmetrizer $\hat{\mathscr{A}}$, electron $(Nsm + i)$ occupies the orbital having $m_j = m$ which is defined by the label i. The quantity Nsm is defined to be zero when $m = m_{\min}$, the smallest m_j value appearing in (3.9); otherwise it is given by $\sum_{m'=m_{\min}}^{m-1} Nsm'$. For homonuclear systems, unique specification of each orthonormal outer-core orbital in (3.9) is achieved through the definitions

$$\left.\begin{aligned} |\phi_{ncm+2i-1}\, m\rangle &= |\phi_{(ncm+i)+}\, m\rangle; \\ |\phi_{ncm+2i}\, m\rangle &= |\phi_{(ncm+i)-}\, m\rangle. \end{aligned}\right\} \tag{3.10}$$

Because it is subsequently convenient to have a single notation for all the orbitals entering (3.9), the quantity

$$|\phi_i\, m\rangle = |u_i\, \kappa_i\, m\rangle; \quad i \leqslant ncm, \tag{3.11}$$

can be defined.

The atomic orbitals (2.3), (3.2) and (3.3) generated by the Oxford MCDF program consist of numerically defined radial functions multiplied by an analytic space–spin function. Hence each orthonormal orbital entering (3.9) can be expressed as a sum of space–spin functions, with varying κ and centre, each associated with new upper and lower radial functions formed by summing the separate radial contributions generated by the orthogonalization step

$$|\phi_j\, m\rangle = \sum_\kappa \sum_\mu |\Omega_{j\mu\kappa m}\rangle, \tag{3.12}$$

where
$$|\Omega_{j\mu\kappa m}\rangle = \sum_i U_{ij\,m} |u_i\, \kappa_i\, m\rangle\, \delta_{\mu,\mu_i}\, \delta_{\kappa,\kappa_i}. \tag{3.13}$$

Here U_{ijm} are the elements of the orthogonalization matrix associated with the set of orbitals with a particular m value, and μ_i is the centre of the function $|u_i\, \kappa_i\, m\rangle$, i.e.

$$|\phi_j\, m\rangle = \sum_i U_{ij\,m} |u_i\, \kappa_i\, m\rangle. \tag{3.14}$$

Note that U_{ijm} is unit diagonal for $i \leqslant ncm$.

Here it should be noted that it is computationally much more convenient wherever possible to add orbitals together and then integrate over the combined function, rather than to perform separate integrations over the individual orbitals. This dictates the way in which the interaction energy is calculated.

(*b*) *Symmetry properties of the orthonormal orbitals*

It is shown in this subsection that the molecular outer-core orbitals (3.4)–(3.7) transform under $\hat{H}_{q,\,t}$ and $\hat{T}_{\mathrm{R}}$ in exactly the same way (see (2.15)–(2.18)) as the atomic orbitals (2.3). It then follows, by using the identical arguments that matrix elements involving molecular outer-core orbitals are related in the same ways (equations (2.19) and (2.20)) as those involving atomic orbitals (2.3). Although molecular outer-core orbitals are not eigenfunctions of $\hat{j}^2$ and therefore do not carry the labels j, κ or a, there is a one-to-one correspondence between these orbitals and the atomic orbitals in the ordered list (3.2). Thus the molecular outer-core orbital $|\phi_i\, m\rangle$ (this is $|\phi_{\mu,\,i}\, m\rangle$ for a homonuclear system) is uniquely associated with the atomic orbital $|u_i\, k_i\, m\rangle$ ($|u_{\mu,\,i}\, k_i\, m\rangle$), which is absent from all previous molecular outer-core orbitals $|\phi_j\, m\rangle$ ($|\phi_{\mu,\,j}\, m\rangle$) $(j<i)$, so that $|\phi_i\, m\rangle$ ($|\phi_{\mu,\,i}\, m\rangle$) is the first molecular outer-core orbital to contain $|\mu_i\, k_i\, m\rangle$ ($|u_{\mu,\,i}\, k_i\, m\rangle$). Hence the labels j_i and a_i, which appear in relations of the type (2.15)–(2.20) obeyed by molecular outer-core orbitals, are the quantum numbers of the atomic orbital $|u_{\mu,\,i}\, k_i\, m\rangle$ with the molecular outer-core orbital is uniquely associated.

For homonuclear and heteronuclear systems respectively the first orthonormal outer-core orbitals $|\phi_i - |m|\rangle$ with $i = ncm+1$ are defined by (3.4) and (3.8) respectively, with a negative value for the m_j quantum number. Application of either $\hat{H}_{y,\,t}$ or $\hat{T}_{\mathrm{R}}$ onto the orthonormal outer-core orbital $|\phi_i\, m\rangle$ having a positive m_j quantum number and invoking (2.19*a*) shows that

$$\hat{T}_{\mathrm{R}}|\phi_i\, m\rangle = \hat{H}_{y,\,t}|\phi_i\, m\rangle = (-1)^{m+\frac{1}{2}}\,(-1)^{\frac{1}{2}(1-a_i)}\,|\phi_i - m\rangle; \quad i = ncm+1, \tag{3.15}$$

whence it follows from $\hat{H}^{\dagger}_{y,\,t}\,\hat{H}_{y,\,t} = 1$ that

$$\langle\phi_i - m\,|u_{\mu,\,j}\,\kappa_j - m\rangle = (-1)^{\frac{1}{2}(a_i-a_j)}\,\langle\phi_i\, m\,|u_{\mu,\,j}\,\kappa_j\, m\rangle. \tag{3.16}$$

Application of either $\hat{H}_{y,\,t}$ or $\hat{T}_{\mathrm{R}}$ onto the second orthonormal outer-core orbital (3.5) or (3.8) followed by invoking (2.19*a*) and (3.16) shows that

$$\hat{T}_{\mathrm{R}}|\phi_i\, m\rangle = \hat{H}_{y,\,t}\,|\phi_i\, m\rangle = (-1)^{m+\frac{1}{2}}(-1)^{\frac{1}{2}(1-a_i)}\,|\phi_i - m\rangle. \tag{3.17}$$

It then follows from $\hat{H}^{\dagger}_{q,\,t}\,\hat{H}_{q,\,t} = 1$ that

$$\langle\phi_i - m\,|\phi_j - m\rangle = (-1)^{\frac{1}{2}(a_i-a_j)}\,\langle\phi_i\, m|\phi_j\, m\rangle; \tag{3.18a}$$

$$\langle\phi_i - m|\hat{\mathscr{H}}_{\mathrm{KE}}|\phi_j - m\rangle = (-1)^{\frac{1}{2}(a_i-a_j)}\,\langle\phi_i\, m|\hat{\mathscr{H}}_{\mathrm{KE}}|\phi_j\, m\rangle; \tag{3.18b}$$

$$\langle\phi_i - m|\hat{V}_{\mathrm{nuc}}|\phi_j - m\rangle = (-1)^{\frac{1}{2}(a_i-a_j)}\,\langle\phi_i\, m|\hat{V}_{\mathrm{nuc}}|\phi_j\, m\rangle; \tag{3.18c}$$

$$\langle\phi_i\, m\,\phi_j\, m'|r_{12}^{-1}|\phi_k\, m''\,\phi_l\, m'''\rangle = (-1)^{\frac{1}{2}(a_i+a_j-a_k-a_l)}\,\langle\phi_i - m\phi_j - m'|r_{12}^{-1}|\phi_k - m''\,\phi_l - m'''\rangle. \tag{3.19}$$

It is trivial to prove by induction that the relations (3.16)–(3.19) are valid for all orthonormal outer-core orbitals, (3.16) being non-zero only for $j > ncm$. Identical arguments show (3.16)–(3.19) to be valid for the molecular outer-core orbitals (3.6) and (3.7) in a homonuclear system. In the standard expansion (5.4) (Brink & Satchler 1968) of r_{12}^{-1}, only terms independent of the azimuthal angles ϕ_1 and ϕ_2 contribute to integrals of the type $\langle\phi_i\, m\,\phi_j\, m'|r_{12}^{-1}|\phi_k\, m\,\phi_l\, m'\rangle$. Hence, for these integrals, one can write

$$\begin{aligned}\langle\phi_i\, m\,\phi_j\, m'|r_{12}^{-1}|\phi_k\, m\,\phi_l\, m'\rangle &= \langle\phi_i\, m\,\phi_j\, m'|r_{12}^{-1}\,\hat{H}^{\dagger}_{y,\,t}(1)\,\hat{H}_{y,\,t}(1)\,|\phi_k\, m\,\phi_l\, m'\rangle\\ &= \langle\phi_i\, m\,\phi_j\, m'|\hat{H}^{\dagger}_{y,\,t}(1)\,r_{12}^{-1}\,\hat{H}_{y,\,t}(1)\,|\phi_k\, m\,\phi_l\, m'\rangle,\end{aligned} \tag{3.20}$$

because the operator $\hat{H}_{y,\,s}(1)$ for reflection of the coordinates of electron 1 in the xz plane changes ϕ_1 to $-\phi_1$, while (3.20) has no contributions from terms in r_{12}^{-1} depending on this angle. Substitution of (3.17) into (3.20) then establishes

$$\begin{aligned}\langle \phi_i\, m\, \phi_j\, m' | r_{12}^{-1} | \phi_k\, m\, \phi_l\, m' \rangle &= (-1)^{\frac{1}{2}(a_i - a_k)} \langle \phi_i - m\, \phi_j\, m' | r_{12}^{-1} | \phi_k - m\, \phi_l\, m' \rangle \\ &= (-1)^{\frac{1}{2}(a_j - a_l)} \langle \phi_i\, m\, \phi_j - m' | r_{12}^{-1} | \phi_k\, m\, \phi_l - m' \rangle. \end{aligned} \tag{3.21}$$

where the second relation is derived from the form of (3.20) containing $\hat{H}_{y,\,t}(2)$. The relations (3.21) are also satisfied by the two-electron integrals over pure central field orbitals (3.2).

The approach used to derive (3.17) also shows that, in a homonuclear system, the molecular outer-core orbitals (3.6) and (3.7) are transformed under $\hat{H}_{z,\,t}$ in exactly the same way as the central field orbitals (3.2). Thus, left multiplication of (3.6) by $\hat{H}_{z,\,t}$ and then invoking (2.20) shows that the first molecular outer-core orbitals (3.6) also have this property. The use of $\hat{H}^{\dagger}_{z,\,t}\,\hat{H}_{z,\,t} = 1$ then yields

$$\langle u_{\mu,\,i}\, \kappa_i\, m | \phi_{\mu',\,h}\, m \rangle = (-1)^{j_h - j_i} (-1)^{\frac{1}{2}(a_i - a_h)} \langle u_{\mu',\,i}\, \kappa_i\, m | \phi_{\mu,\,h}\, m \rangle, \quad (\mu' \neq \mu). \tag{3.22}$$

Application of $\hat{H}_{z,\,t}$ to the second molecular outer-core orbitals (3.7) shows after the use of (2.20) and (3.22) that

$$\hat{H}_{z,\,t} | \phi_{\mu,\,i}\, m \rangle = i(-1)^{j_i - m + \frac{1}{2}(1 - a_i)} | \phi_{\mu',\,i}\, m \rangle, \quad (\mu' \neq \mu). \tag{3.23}$$

A simple proof by induction then establishes the validity of (3.22) and (3.23) for all molecular outer-core orbitals, (3.22) being non-zero only for $i > \frac{1}{2}ncm$.

The two-electron integrals can be expressed as the energy of repulsion between two charge densities:

$$\langle \phi_i\, m\, \phi_j\, m' | r_{12}^{-1} | \phi_k\, m''\, \phi_l\, m''' \rangle = \iint D^{(i,\, m,\, k,\, m'')}(\boldsymbol{r}_1)\, D^{(j,\, m',\, l,\, m''')}(\boldsymbol{r}_2)\, r_{12}^{-1}\, \mathrm{d}\boldsymbol{r}_1\, \mathrm{d}\boldsymbol{r}_2, \tag{3.24}$$

where the charge densities are defined by

$$D^{(i,\, m,\, k,\, m'')}(\boldsymbol{r}) = [\phi_i\, m(\boldsymbol{r})]^{+} [\phi_k\, m''(\boldsymbol{r})]. \tag{3.25}$$

Left multiplication of (3.17) by $-i\Sigma_2$ and the use of (2.13) shows that

$$[\phi_i\, m(\boldsymbol{r})]^{*} = (-1)^{m + \frac{1}{2}} (-1)^{\frac{1}{2}(1 - a_i)} (-i\Sigma_2) (\phi_i - m). \tag{3.26}$$

When taken in conjunction with

$$[\phi_i\, m(\boldsymbol{r})]^{+} = \{[\phi_i\, m(\boldsymbol{r})]^{*}\}^{\mathrm{T}}, \tag{3.27}$$

where T denotes the transpose, this establishes that

$$D^{(i,\, m,\, k,\, m'')}(\boldsymbol{r}) = (-1)^{m'' - m} (-1)^{\frac{1}{2}(a_k - a_i)} D^{(k,\, -m'',\, i,\, -m)}(\boldsymbol{r}); \tag{3.28}$$

whence

$$\begin{aligned}\langle \phi_i\, m\, \phi_j\, m' | r_{12}^{-1} | \phi_k\, m''\, \phi_l\, m''' \rangle &= (-1)^{m'' - m} (-1)^{\frac{1}{2}(a_k - a_i)} \langle \phi_k - m''\, \phi_j\, m' | r_{12}^{-1} | \phi_i - m\, \phi_l\, m''' \rangle \\ &= (-1)^{m''' - m'} (-1)^{\frac{1}{2}(a_l - a_j)} \langle \phi_i\, m\, \phi_l - m''' | r_{12}^{-1} | \phi_k\, m''\, \phi_j - m' \rangle. \end{aligned} \tag{3.29}$$

A special case of (3.29) shows that

$$\langle \phi_i\, m\, \phi_j\, m' | r_{12}^{-1} | \phi_i - m\, \phi_l\, m''' \rangle = 0. \tag{3.30}$$

The transformation property (3.17) of the orthogonal orbitals is important because it shows the wavefunction (3.1), (3.9) to be symmetric under the many-electron generalizations (equation (2.19) of Pyper (1982)) of the operators $\hat{H}_{x,\,t}$, $\hat{H}_{y,\,t}$ and time reversal, while (3.23) shows this to be also symmetric under the many-electron generalization of $\hat{H}_{z,\,t}$. Any trustworthy approximation to the exact wavefunction should have these properties possessed by the latter (Pyper 1982). The relations between the integrals derived in this section are used to simplify the calculation of the energy of the wavefunction (3.9), (3.1).

(c) *Calculation of the interaction energy*

(i) *Complete energy expression*

It is inappropriate to calculate $\langle \Psi | \mathscr{H}_{\mathrm{T}} | \Psi \rangle$ directly because this quantity is, in general, very large (typically 20000 a.u.), while the quantity of chemical interest, namely the change in energy on formation of the molecule, is very small (typically 0.1 a.u.). Most of the contribution to $\langle \Psi | \mathscr{H}_{\mathrm{T}} | \Psi \rangle$ comes from the 'inner'-core orbitals, and because these are unchanged in the molecular environment it is clearly sensible to perform the calculation in such a way that most of the terms involving the 'inner' core are removed. This is done by calculating the interaction energy $\Delta E^{\mathrm{int}}_{\mathrm{core}}$, which is simply the difference between the energy of the molecule and the sum of the energies of the constituent atoms:

$$\Delta E^{\mathrm{int}}_{\mathrm{core}} = \langle \Psi | \mathscr{H}_{\mathrm{TOT}} | \Psi \rangle - \langle \Phi_1 | \mathscr{H}_{\mathrm{T1}} | \Phi_1 \rangle - \langle \Phi_2 | \mathscr{H}_{\mathrm{T2}} | \Phi_2 \rangle, \tag{3.31}$$

where
$$\mathscr{H}_{\mathrm{TOT}} = \mathscr{H}_{\mathrm{T}} + Z_1 Z_2 / R,$$
$$\mathscr{H}_{\mathrm{T}\mu} = \sum_{i=1}^{N\mu} (\mathscr{H}_{\mathrm{KE}}(i) - Z_\mu / r_{\mu,\,i}) + \sum_{i=1}^{(N\mu)-1} \sum_{j=i+1}^{N\mu} r_{ij}^{-1}, \tag{3.32}$$

where Z_μ is the charge on nucleus μ and R is the separation of the two nuclei.

The wavefunction (3.9) for the interacting system and those of isolated atoms can be written

$$\left.\begin{aligned} |\Psi(\boldsymbol{r}_1, \ldots \boldsymbol{r}_N)\rangle &= \hat{\mathscr{A}}\Big(\prod_m \prod_{j=1}^{Nm} |\phi_j m\rangle\Big), \\ |\Phi_\mu(\boldsymbol{r}_1, \ldots \boldsymbol{r}_{n\mu}\rangle &= \hat{\mathscr{A}}\Big(\prod_m \prod_{j=1}^{N\mu m} |u_{\mu,\,j}\,\kappa_j\, m\rangle\Big), \end{aligned}\right\} \tag{3.33}$$

where the notation (3.3) is used for the atomic orbitals and $N\mu m$ is the total number of inner- plus outer-core orbitals on atom μ having $m_j = m$. Substitution of (3.33) and (3.32) into (3.31) shows, from standard techniques, that

$$\begin{aligned} \Delta E^{\mathrm{int}}_{\mathrm{core}} = {} & \sum_m \sum_{i=1}^{Nm} \langle \phi_i\, m | \mathscr{H}_{\mathrm{KE}} - Z_1/r_1 - Z_2/r_2 | \phi_i\, m\rangle + Z_1 Z_2 / R \\ & + \frac{1}{2} \sum_m \sum_{m'} \sum_{i=1}^{Nm} \sum_{j=1}^{Nm'} (\langle \phi_i\, m\, \phi_j\, m' | r_{12}^{-1} | \phi_i\, m\, \phi_j\, m'\rangle - \langle \phi_i\, m\, \phi_j\, m' | r_{12}^{-1} | \phi_j\, m'\, \phi_i\, m\rangle) \\ & - \sum_m \sum_{i=1}^{N1m} \langle u_{1,\,i}\, \kappa_i\, m | \hat{\mathscr{H}}_{\mathrm{KE}} - Z_1/r_1 | u_{1,\,i}\, \kappa_i\, m\rangle \\ & - \frac{1}{2} \sum_m \sum_{m'} \sum_{i=1}^{N1m} \sum_{j=1}^{N1m'} (\langle u_{1,\,i}\, \kappa_i\, m\, u_{1,\,j}\, \kappa_j\, m' | r_{12}^{-1} | u_{1,\,i}\, \kappa_i\, m\, u_{1,\,j}\, \kappa_j\, m'\rangle \\ & - \langle u_{1,\,i}\, \kappa_i\, m\, u_{1,\,j}\, \kappa_j\, m' | r_{12}^{-1} | u_{1,\,j}\, \kappa_j\, m'\, u_{1,\,i}\, \kappa_i\, m\rangle) \\ & - \sum_m \sum_{i=1}^{N2m} \langle u_{2,\,i}\, \kappa_i\, m | \hat{\mathscr{H}}_{\mathrm{KE}} - Z_2/r_2 | u_{2,\,i}\, \kappa_i\, m\rangle \\ & - \frac{1}{2} \sum_m \sum_{m'} \sum_{i=1}^{N2m} \sum_{j=1}^{N2m'} (\langle u_{2,\,i}\, \kappa_i\, m\, u_{2,\,j}\, \kappa_j\, m' | r_{12}^{-1} | u_{2,\,i}\, \kappa_i\, m\, u_{2,\,j}\, \kappa_j\, m'\rangle \\ & - \langle u_{2,\,i}\, \kappa_i\, m\, u_{2,\,j}\, \kappa_j\, m' | r_{12}^{-1} | u_{2,\,j}\, \kappa_j\, m'\, u_{2,\,i}\, \kappa_i\, m\rangle) \end{aligned} \tag{3.34a}$$

$$\equiv \Delta E_{\mathrm{KE}} + \Delta E_{\mathrm{NC}} + \Delta E_{\mathrm{EX}}. \tag{3.34b}$$

In the one-electron integrals, r_μ is the distance of the electron from nucleus μ, while r_{12} in the two-electron integrals is the distance between electrons 1 and 2. The interaction energy (3.34*a*) is decomposed (3.34*b*) into a kinetic energy term (ΔE_{KE}), a nuclear–coulomb term (ΔE_{NC}) involving the electron–nuclear attractions plus the direct ('coulomb') electron–electron repulsion integrals ($\langle\phi_i\,\phi_j|r_{12}^{-1}|\phi_i\,\phi_j\rangle$), and an exchange term (ΔE_{EX}) consisting of exchange integrals $\langle\phi_i\,\phi_j|r_{12}^{-1}|\phi_j\,\phi_i\rangle$. The kinetic energies and attractions for their own nuclei of inner-core electrons, together with intra-atomic inner-core electron–electron repulsions, are the largest terms in (3.34*a*). However these contributions, appearing in the sums over orthonormal orbitals $|\phi_i\,m\rangle$ to the energy of the molecule are the same as those to the energies of the isolated atoms, appearing in the sums over atomic orbitals (3.3).

(ii) *The kinetic energy term*

The kinetic energy term from (3.34) is, after noting that the inner-core contributions in the molecule exactly cancel those in the free atoms,

$$\Delta E_{\mathrm{KE}} = \sum_{m}\sum_{i=ncm+1}^{Nm}\langle\phi_i\,m|\mathscr{H}_{\mathrm{KE}}|\phi_i\,m\rangle - \sum_{m}\sum_{i=nc1m+1}^{N1m}\langle u_{1,\,i}\,\kappa_i\,m|\hat{\mathscr{H}}_{\mathrm{KE}}|u_{1,\,i}\,\kappa_i\,m\rangle$$
$$-\sum_{m}\sum_{i=nc2m+1}^{N2m}\langle u_{2,\,i}\,\kappa_i\,m|\hat{\mathscr{H}}_{\mathrm{KE}}|u_{2,\,i}\,\kappa_i\,m\rangle. \qquad (3.35)$$

The summation over the orthonormal orbitals ($|\phi_i\,m\rangle$) of the molecule may be restricted to positive m values by using (3.18*b*). The summations over the m_j quantum numbers in the kinetic energies of the outer-core orbitals in the isolated atoms (the last two lines) can be evaluated analytically (Grant 1970) to yield

$$\Delta E_{\mathrm{KE}} = 2\sum_{m>0}\sum_{i=ncm+1}^{Nm}\langle\phi_i\,m|\mathscr{H}_{\mathrm{KE}}|\phi_i\,m\rangle - \sum_{A\epsilon 0c1}(2j_A+1)\,I_{\mathrm{KE}}(A) - \sum_{B\epsilon 0c2}(2j_B+1)\,I_{\mathrm{KE}}(B). \qquad (3.36)$$

The summations over A and B are over all the subshells in the outer cores of atoms 1 and 2 respectively, while $I_{\mathrm{KE}}(A)$ is an atomic relativistic kinetic energy integral, the computation of which is simple and standard (Grant 1970).

The integrals yielding the kinetic energies of the orthonormal outer-core orbitals in the molecule are not computed directly, but generated by transforming the kinetic energy integrals over the original atomic orbitals

$$\langle\phi_i\,m|\mathscr{H}_{\mathrm{KE}}|\phi_j\,m\rangle = \sum_{s}\sum_{t}U_{sim}\,U_{tjm}\langle u_s\,\kappa_s\,m|\hat{\mathscr{H}}_{\mathrm{KE}}|u_t\,\kappa_t\,m\rangle. \qquad (3.37)$$

The computation of these two-centre kinetic energy integrals over atomic orbitals is described in §5.

(iii) *The nuclear attraction and coulomb terms*

The nuclear attraction and 'direct' electron–electron repulsions are grouped together into the term ΔE_{NC} because they involve similar quantities which to a large extent, tend to cancel. After noting that the purely inner-core contributions to ΔE_{NC} in the molecule cancel those of the isolated atoms, (3.34) shows that

$$\Delta E_{\mathrm{NC}} = \Delta E_{\mathrm{NCM}} + \Delta E_{\mathrm{CLM}} + \Delta E_{\mathrm{NCA}} + Z_1\,Z_2/R; \qquad (3.38)$$

$$\Delta E_{\mathrm{NCM}}=\sum_{m}\sum_{i=ncm+1}^{Nm}\Big(\langle\phi_i\,m|-Z_1/r_1-Z_2/r_2|\phi_i\,m\rangle+\sum_{m'}\sum_{j=1}^{ncm'}\langle\phi_i\,m\,\phi_j\,m'|r_{12}^{-1}|\phi_i\,m\,\phi_j\,m'\rangle\Big);\tag{3.39}$$

$$\Delta E_{\mathrm{CLM}}=\frac{1}{2}\sum_{m}\sum_{i=ncm+1}^{Nm}\sum_{m'}\sum_{j=ncm'+1}^{Nm'}\langle\phi_i\,m\,\phi_j\,m'|r_{12}^{-1}|\phi_i\,m\phi_j\,m'\rangle;\tag{3.40}$$

$$\begin{aligned}\Delta E_{\mathrm{NCA}}=&\sum_{m}\sum_{i=1}^{nc1m}\langle u_{1,\,i}\,\kappa_i\,m|-Z_2/r_2|u_{1,\,i}\,\kappa_i\,m\rangle+\sum_{m}\sum_{i=1}^{nc2m}\langle u_{2,\,i}\,\kappa_i\,m|-Z_1/r_1|u_{2,\,i}\,\kappa_i\,m\rangle\\&-\sum_{m}\sum_{i=nc1m+1}^{N1m}\langle u_{1,\,i}\,\kappa_i\,m|-Z_1/r_1|u_{1,\,i}\,\kappa_i\,m\rangle-\sum_{m}\sum_{i=nc2m+1}^{N2m}\langle u_{2,\,i}\,\kappa_i\,m|-Z_2/r_2|u_{2,\,i}\,\kappa_i\,m\rangle\\&+\sum_{m}\sum_{m'}\sum_{i=1}^{nc1m}\sum_{j=1}^{nc2m'}\langle u_{1,\,i}\,\kappa_i\,m\,u_{2,\,j}\,\kappa_j\,m'|r_{12}^{-1}|u_{1,\,i}\,\kappa_i\,m\,u_{2,\,j}\,\kappa_j\,m'\rangle\\&-\frac{1}{2}\sum_{m}\sum_{m'}\sum_{i=nc1m+1}^{N1m}\Big(\sum_{j=nc1m'+1}^{N1m'}\langle u_{1,\,i}\,\kappa_i\,m\,u_{1,\,j}\,\kappa_j\,m'|r_{12}^{-1}|u_{1,\,i}\,\kappa_i\,m\,u_{1,\,j}\,\kappa_j\,m'\rangle\\&+2\sum_{j=1}^{nc1m'}\langle u_{1,\,i}\,\kappa_i\,m\,u_{1,\,j}\,\kappa_j\,m'|r_{12}^{-1}|u_{1,\,i}\,\kappa_i\,m\,u_{1,\,j}\,\kappa_j\,m'\rangle\Big)\\&-\frac{1}{2}\sum_{m}\sum_{m'}\sum_{i=nc2m+1}^{N2m}\Big(\sum_{j=nc2m'+1}^{N2m'}\langle u_{2,\,i}\,\kappa_i\,m\,u_{2,\,j}\,\kappa_j\,m'|r_{12}^{-1}|u_{2,\,i}\,\kappa_i\,m\,u_{2,\,j}\,\kappa_j\,m'\rangle\\&+2\sum_{j=1}^{nc2m'}\langle u_{2,\,i}\,\kappa_i\,m\,u_{2,\,j}\,\kappa_j\,m'|r_{12}^{-1}|u_{2,\,i}\,\kappa_i\,m\,u_{2,\,j}\,\kappa_j\,m'\rangle\Big).\end{aligned}\tag{3.41}$$

The first contribution (ΔE_{NCM}) to ΔE_{NC} comprises the attraction to the nuclei of the orthonormal outer-core orbitals in the molecule plus the coulombic (direct) repulsion between this outer core and the inner core. Because (3.18*c*) shows that the summation over the orthonormal outer-core orbitals can be restricted to positive values of m, ΔE_{NCM} becomes

$$\Delta E_{\mathrm{NCM}}=2\sum_{m>0}\langle\phi_i\,m|\Big(-Z_1/r_1-Z_2/r_2+\sum_{m'}\sum_{j=1}^{ncm'}\langle\phi_j\,m'|r_{12}^{-1}|\phi_j\,m'\rangle\Big)|\phi_i\,m\rangle,\tag{3.42}$$

where the third operator term is the electrostatic potential generated by the inner-core orbitals. It is a standard result (Grant 1970) that the potential ($\hat{V}_{\mu\mathrm{core}}(r_\mu)$) generated by the nucleus plus the core of atom μ is a spherically symmetric function centred on the nucleus of μ and is given by

$$\begin{aligned}\hat{V}_{\mu\mathrm{core}}(r_\mu)&=-Z_\mu/r_\mu+\sum_{m'}\sum_{i=1}^{nc1m'}\langle\phi_j\,m'|r_{12}^{-1}|\phi_j\,m'\rangle\\&=-Z_\mu/r_\mu+\sum_{A\in Ic\mu}(2j_A+1)\int_0^\infty\left[P_A^2(r'_\mu)+Q_A^2(r'_\mu)\right]r_{\mu>}^{-1}\,\mathrm{d}r'_\mu,\end{aligned}\tag{3.43}$$

where the sum over A is over all the inner-core subshells of atom μ, and $r_{\mu>}$ is the greater of r_μ and r'_μ. As with the kinetic energy terms, the integrals entering (3.42) are evaluated by first computing the matrix, having elements V_{st}, over atomic outer-core orbitals:

$$V_{st}=\langle u_s\,\kappa_s\,m|\hat{V}_{1\mathrm{core}}(r_1)+\hat{V}_{2\mathrm{core}}(r_2)\,|u_t\,\kappa_t\,m\rangle,\tag{3.44}$$

and then transforming to the orthonormal outer-core orbital representation. The computation of both the potentials (3.43) and those portions of the integrals (3.44) located entirely on one nucleus is standard (Grant 1970), while the calculation of the two centred terms in (3.44) is described in §5.

The result (3.21) shows that the second term (ΔE_{CLM}) in (3.38), which is the coulomb repulsion between the outer-core electrons in the molecule, can be written:

$$\Delta E_{\mathrm{CLM}} = 2 \sum_{m>0} \sum_{i=ncm+1}^{Nm} \left\langle \phi_i\, m \middle| \left(\sum_{m'>0} \sum_{j=ncm'+1}^{Nm'} \langle \phi_j\, m' | r_{12}^{-1} | \phi_j\, m' \rangle \right) \middle| \phi_i\, m \right\rangle. \tag{3.45}$$

This is evaluated by first computing the potential generated by the density

$$\sum_{m'>0} \sum_{j=ncm'+1}^{Nm'} [\phi_j\, m'(\boldsymbol{r})]^{+} \, [\phi_j\, m'(\boldsymbol{r})],$$

which is independent of i and m, and then calculating the energy of interaction of this density with the potential just calculated. The quantity ΔE_{CLM} contains a self-energy term (ΔE_{SELF}), given by

$$\Delta E_{\mathrm{SELF}} = \sum_{m>0} \sum_{i=ncm+1}^{Nm} \langle \phi_i\, m\, \phi_i\, m | r_{12}^{-1} | \phi_i\, m\, \phi_i\, m \rangle, \tag{3.46}$$

which is cancelled by a similar term in the exchange energy, ΔE_{EX}. Each individual term in the self-energy is computed by using similar techniques at the same time as ΔE_{CLM}, rather than as part of the exchange energy. The computational techniques used for both ΔE_{CLM} and ΔE_{SELF} are described in §5.

The third term (ΔE_{NCA}) in (3.38) involves only central field atomic orbitals (2.3). Furthermore all the terms, excepting the first, second and fifth, are purely one-centred and can therefore be evaluated by using standard techniques (Grant 1970). The fifth term, being the purely coulombic repulsion between the cores of atoms 1 and 2 which have negligible overlap, is given by $(Nc_1)\,(Nc_2)/R$, where Nc_μ is the number of inner-core orbitals on atom μ. Thus ΔE_{NCA} becomes

$$\begin{aligned} \Delta E_{\mathrm{NCA}} = {} & \sum_{m} \sum_{i=1}^{nc1m} \langle u_{1,\,i}\, \kappa_i\, m | -Z_2/r_2 | \, u_{1,\,i}\, \kappa_i\, m \rangle + \sum_{m} \sum_{i=1}^{nc2m} \langle u_{2,\,i}\, \kappa_i\, m | -Z_1/r_1 | \, u_{2,\,i}\, \kappa_i\, m \rangle \\ & + (Nc_1)\,(Nc_2)/R - \sum_{A \epsilon 0c1} (2j_A+1)\, I_v(A) - \sum_{B \epsilon 0c2} (2j_B+1)\, I_v(B) \\ & - \frac{1}{2} \sum_{A \epsilon 1} \sum_{A' \epsilon 0c1} (2j_A+1)\,(2j_{A'}+1)\,(2-\delta_{A_0\,A_0'})\, F_c^0(A, A') \\ & - \frac{1}{2} \sum_{B \epsilon 2} \sum_{B' \epsilon 0c2} (2j_B+1)\,(2j_{B'}+1)\,(2-\delta_{B_0\,B_0'})\, F_c^0(B, B') \end{aligned} \tag{3.47}$$

where $F_c^0(A, A')$ is an atomic relativistic radial direct electron–electron repulsion integral (Grant 1970, equation 8.3) and $I_v(A)$ is the atomic nuclear attraction integral

$$I_v(A) = -\int_0^\infty [Z_\mu (P_A^2(r_\mu) + Q_A^2(r_\mu))]\, r_\mu^{-1}\, \mathrm{d}r_\mu \tag{3.48}$$

In (3.47) the sums over A and B are over all the subshells belonging to atoms 1 and 2 respectively and $\delta_{A_0 A_0'}$ is one if both subshells A and A' belong to the outer core and is zero otherwise. The first two terms in (3.47) can be evaluated by using the methods described in §5, although it is consistent with the above calculation of the repulsion between the two inner cores to express these as $-Z_2(Nc_1)/R$ and $-Z_1(Nc_2)/R$ respectively.

(iv) *The exchange energy*

The exchange contribution (ΔE_{EX}) to the interaction energy (3.34) becomes, after noting that the purely inner core contributions in the molecule cancel those of the isolated atoms,

$$\Delta E_{\mathrm{EX}} = \Delta E_{\mathrm{EXM}} + \Delta E_{\mathrm{EXA}} \tag{3.49}$$

$$\begin{aligned}\Delta E_{\mathrm{EXM}} = &-\frac{1}{2}\sum_{m}\sum_{m'}\sum_{i=ncm+1}^{Nm}\sum_{j=ncm'+1}^{Nm'} \langle \phi_i\, m\, \phi_j\, m' | r_{12}^{-1} | \phi_j\, m'\, \phi_i\, m\rangle \\ &-\sum_{m}\sum_{m'}\sum_{i=ncm+1}^{Nm}\sum_{j=1}^{ncm'} \langle \phi_i\, m\, \phi_j\, m' | r_{12}^{-1} | \phi_j\, m'\, \phi_i\, m\rangle.\end{aligned} \tag{3.50}$$

$$\begin{aligned}\Delta E_{\mathrm{EXA}} = &\frac{1}{2}\sum_{m}\sum_{m'}\sum_{i=nc1m+1}^{N1m}\sum_{j=nc1m'+1}^{N1m'} \langle u_{1,\,i}\,\kappa_i\, m\, u_{1,\,j}\,\kappa_j\, m' | r_{12}^{-1} | u_{1,\,j}\,\kappa_j\, m'\, u_{1,\,i}\,\kappa_i\, m\rangle \\ &+\sum_{m}\sum_{m'}\sum_{i=1}^{nc1m}\sum_{j=nc1m+1}^{N1m'} \langle u_{1,\,i}\,\kappa_i\, m\, u_{1,\,j}\,\kappa_j\, m' | r_{12}^{-1} | u_{1,\,j}\,\kappa_j\, m'\, u_{1,\,i}\,\kappa_i\, m\rangle \\ &+\frac{1}{2}\sum_{m}\sum_{m'}\sum_{i=nc2m+1}^{N2m}\sum_{j=nc2m'+1}^{N2m'} \langle u_{2,\,i}\,\kappa_i\, m\, u_{2,\,j}\,\kappa_j\, m' | r_{12}^{-1} | u_{2,\,j}\,\kappa_j\, m'\, u_{2,\,i}\,\kappa_i\, m\rangle \\ &+\sum_{m}\sum_{m'}\sum_{i=1}^{nc2m}\sum_{j=nc2m'+1}^{N2m'} \langle u_{2,\,i}\,\kappa_i\, m\, u_{2,\,j}\,\kappa_j\, m' | r_{12}^{-1} | u_{2,\,j}\,\kappa_j\, m'\, u_{2,\,i}\,\kappa_i\, m\rangle.\end{aligned} \tag{3.51}$$

The exchange terms between the inner-core orbitals on one centre and those on the other centre are neglected because the differential overlaps between such orbitals are vanishingly small.

The result (3.19) shows that the summations over m, but not m', in the molecular contribution (3.50) can be restricted to positive m, the coefficient of each term being doubled. The terms in (3.50) having simultaneously $i = j$ and $m = m'$ constitute the self-energy (3.46), which has already been calculated. The methods used to compute the remaining terms of (3.50) are described in §5.

The remaining contribution to ΔE_{EX} consists of that portion (ΔE_{EXA}) of the exchange energy of the isolated atoms which changes in the molecule because it involves the outer-core orbitals of the free atoms. Evaluation of these purely atomic terms yields (Grant 1970):

$$\begin{aligned}\Delta E_{\mathrm{EXA}} = \sum_{\mu=1,\,2}\Bigg[&\sum_{A\epsilon 0c\mu} (j_A+\tfrac{1}{2})\, F_c^0(A,A) \\ &+\frac{1}{2}\sum_{A\epsilon\mu}\sum_{A'\epsilon 0c\mu} (2j_A+1)\,(2j'_A+1)\,(2-\delta_{A_0A'_0}) \sum_{L>0} \Pi(\kappa_A,\kappa_{A'},L) \begin{pmatrix} j_A & j_{A'} & L \\ \frac{1}{2} & -\frac{1}{2} & 0\end{pmatrix}^2 G_c^L(A,A')\Bigg],\end{aligned} \tag{3.52}$$

where $\Pi(\kappa_A,\kappa_{A'},L)$ is a parity selection factor which vanishes unless l_A+l_B+L is even; $G_c^L(A,A')$ is an atomic relativistic radial exchange electron–electron repulsion integral (equation (8.4) of Grant 1970), and $\begin{pmatrix} j_A & j_{A'} & L \\ \frac{1}{2} & -\frac{1}{2} & 0\end{pmatrix}$ is a $3j$ symbol (Brink & Satchler 1968). The first term in (3.52) cancels the self-energy included in the direct repulsion between the outer-core electrons of the free atoms present in ΔE_{NCA} (3.47).

4. VALENCE WAVEFUNCTIONS

The valence portion of the wavefunction (2.1) describes both those electrons occupying open shells in the isolated atoms plus those occupying the core orbitals that are significantly affected by the formation of the molecule. The valence function can be taken to be a single antisymmetrized Hartree product of molecular orbitals when (2.1) becomes a relativistic molecular orbital wavefunction calculated within the frozen core approximation. The computation (Wood 1984) of such wavefunctions for the chlorides of both astatine and the superheavy element with nuclear charge 117 will be described elsewhere. The valence wavefunction can be generalized either by introducing configurations built from excited molecular orbitals, which describe valence electron correlation, or by taking this to be one of the relativistic generalizations of the valence bond method. The RIP program has been used (Wood & Pyper 1981 *a*) to compare molecular orbital, configuration interaction, relativistic valence bond and kappa valence (Pyper 1980 *b*) descriptions of the dimer of element 113. The valence wavefunction of whatever form is built from a set of purely numerically defined central field orbitals (2.3), which includes at least the valence Dirac–Fock atomic orbitals occupied in the isolated atoms.

The calculation of the expectation value of $\mathscr{H}_{\mathrm{T}}$ for the wavefunction (2.1) containing valence electrons is a straightforward extension of the method used for the closed-shell system. The core orbitals are first orthogonalized as described in §3*a*. The wavefunction (2.1) remains unchanged if any linear combinations of the core orbitals are added to the orbitals $|u_{\mathrm{v}i}(\boldsymbol{r})\rangle$ which are used to construct the valence wavefunction. Consequently, each orbital used to form the valence wavefunction can be replaced by a linear combination of that valence orbital with the core orbitals, constructed such that the new valence orbital $|\phi_{\mathrm{v}i}(\boldsymbol{r})\rangle$ is orthogonal to all the core orbitals. With these transformations of the orbitals the wavefunction (2.1) becomes

$$|\Psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)\rangle = \hat{\mathscr{A}}_{\mathrm{cv}}\left\{\hat{\mathscr{A}}_{\mathrm{c}}\left[\prod_{m}\prod_{i=1}^{Nfm} |\phi_i m(\boldsymbol{r}_{Nsm+i})\rangle)\right]|\Phi'_{\mathrm{v}}(\boldsymbol{r}_{nf1+nf2+1}, \ldots, \boldsymbol{r}_N)\rangle\right\}, \tag{4.1}$$

where *Nfm* is the total number of inner- plus outer-core orbitals having $m_j = m$, $\hat{\mathscr{A}}_{\mathrm{c}}$ is the antisymmetrizer for the core wavefunction and $\hat{\mathscr{A}}_{\mathrm{cv}}$ is the partial antisymmetrizer which interchanges coordinates between the core and valence functions. Here the new antisymmetric valence function $|\Phi'_{\mathrm{v}}\rangle$ is constructed from the valence orbitals $|\phi_{\mathrm{v}i}\rangle$ which are orthogonal to the core but not to each other. The methods presented in §3*b* show that each valence orbital $|\phi_{\mathrm{v}i}\rangle$ transforms under the operators $\hat{H}_{q,\,t}$ and $\hat{T}_{\mathrm{R}}$ in exactly the same way as the valence atomic orbital from which it is derived. Each orbital $|\phi_{\mathrm{v}i}\rangle$, though containing many core orbitals, contains only one valence atomic orbital (2.3) so that the labels j_i and a_i which appear in the relations of §3*b* are the j and a quantum numbers of this valence atomic orbital (2.3). These symmetry properties of the valence atomic orbitals can be used to ensure that the wavefunction (4.1) has the correct symmetry. Thus, for example, in a homonuclear diatomic molecule, molecular orbitals constructed as linear combinations of the $|\phi_{\mathrm{v}i}\rangle$ will be eigenfunctions of $\hat{H}_{z,\,t}$ of eigenvalue $+i$ or $-i$, just like the exact eigenfunctions of the molecular relativistic Fock operator (Pyper 1982).

The orthogonality between the valence $|\phi_{\mathrm{v}i}\rangle$ and core orbitals ensures that the valence function $|\Phi'_{\mathrm{v}}\rangle$ is strongly orthogonal (McWeeny 1959) to the core. Hence it follows that the difference between the energy of the molecule and the sum of those of the isolated atoms, the interaction energy, is given by

$$\Delta E_{\mathrm{val}}^{\mathrm{int}} = E_{\mathrm{c}} - E_{1\mathrm{c}} - E_{2\mathrm{c}} + E_{\mathrm{v}} - E_{1\mathrm{v}} - E_{2\mathrm{v}}. \tag{4.2}$$

Here $E_{\mu\mathrm{c}}$ and $E_{\mu\mathrm{v}}$ are the energies of the core and valence electrons respectively in the free atom μ, and E_{c} is that of the core of (4.1) in the molecule. The quantity $(E_{\mathrm{c}} - E_{1\mathrm{c}} - E_{2\mathrm{c}})$ is the interaction energy of the atomic cores in (4.1) given by (3.34). The energy (E_{v}) of the valence electrons consists of an effective one-electron energy plus the electrostatic repulsion energy between the valence electrons, which can be expressed as a sum of integrals of the type $\langle \phi_{\mathrm{v}i}\, \phi_{\mathrm{v}j} | r_{12}^{-1} | \phi_{\mathrm{v}s}\, \phi_{\mathrm{v}t} \rangle$. The effect of the core on the valence orbitals, which is included in the valence effective one-electron energy, is taken into account by simply adding to the nuclear potential operator $\hat{V}_{\mathrm{nuc}}(\boldsymbol{r})$ the direct and exchange potentials generated by the core orbitals. Thus the valence effective one-electron energy consists of a sum of integrals of the type $\langle \phi_{\mathrm{v}i} | \hat{F}_1 | \phi_{\mathrm{v}j} \rangle$, defined by

$$\begin{aligned} \langle \phi_{\mathrm{v}i} | \hat{F}_1 | \phi_{\mathrm{v}j} \rangle = \langle \phi_{\mathrm{v}i} | \mathscr{H}_{\mathrm{KE}} + \hat{V}_{\mathrm{nuc}}(\boldsymbol{r}) | \phi_{\mathrm{v}j} \rangle + \sum_{m} \sum_{s=1}^{Nfm} \\ \times \left(\langle \phi_{\mathrm{v}i}\, \phi_s m | r_{12}^{-1} | \phi_{\mathrm{v}j}\, \phi_s m \rangle - \langle \phi_{\mathrm{v}i}\, \phi_s m | r_{12}^{-1} | \phi_s m\, \phi_{\mathrm{v}j} \rangle \right); \end{aligned} \tag{4.3}$$

$$\begin{aligned} \langle \phi_{\mathrm{v}i} | \hat{F}_1 | \phi_{\mathrm{v}j} \rangle = {} & \langle \phi_{\mathrm{v}i} | \mathscr{H}_{\mathrm{KE}} + \hat{V}_{1\mathrm{core}}(r_1) + \hat{V}_{2\mathrm{core}}(r_2) | \phi_{\mathrm{v}j} \rangle \\ & + \langle \phi_{\mathrm{v}i} | \left(2 \sum_{m>0} \sum_{s=ncm+1}^{Nfm} \langle \phi_s m | r_{12}^{-1} | \phi_s m \rangle \right) | \phi_{\mathrm{v}j} \rangle \\ & - \sum_{m} \sum_{s=1}^{nfm} \langle \phi_{\mathrm{v}i}\, \phi_s m | r_{12}^{-1} | \phi_s m\, \phi_{\mathrm{v}j} \rangle. \end{aligned} \tag{4.4}$$

The integrals over the kinetic energy and direct electrostatic potential generated by the nuclei plus inner-core orbitals (the first term in equation (4.4)) are evaluated by transforming the integrals over the original atomic orbitals (2.3). The integrals over the direct potential generated by the outer core (second portion of equation (4.4)) are evaluated by first constructing this potential, which is independent of $|\phi_{\mathrm{v}i}\rangle$ and $|\phi_{\mathrm{v}j}\rangle$ and then calculating the integrals directly in the same way as the outer core electron–electron repulsion (3.45). Each exchange integral entering the last part of (4.4) has to be computed individually using the techniques described in §5.

The method, used in the RIP program, of constructing the molecular wavefunction (4.1) from a set of numerically defined orbitals, which includes the Dirac–Fock atomic orbitals of the constituent atoms, has three advantages. First it avoids the large basis sets that would be needed if the orbitals were expanded in the conventional Slater or gaussian type functions. Thus it has been shown in the non-relativistic case that a basis of Hartree–Fock atomic orbitals augmented by just one additional Slater or Gaussian function of each symmetry on each atom recovers over 90% of the difference between the Hartree–Fock limit energy and that of the molecular orbital wavefunction constructed from a basis of just the occupied Hartree–Fock atomic orbitals (Raffenetti 1973). Although the Hartree–Fock atomic orbitals in this non-relativistic study were expanded in a gaussian basis, no such expansion is used in the RIP program, which evaluates the molecular integrals directly by using purely numerical methods. The second advantage of using a purely numerical basis is that it is straightforward to ensure that the small components of the basis functions bear the correct relation to the large components, so that all the orbitals describe the behaviour of electrons and not positrons in the presence of the molecular Dirac–Fock potential (Dyall *et al.* 1984*a*, *b*). The small components ϕ^S_{vi} of each basis function are related to the large components ϕ^L_{vi} through a relation of the form

$$\phi^S_{vi} = c^{-1}[2+(\epsilon-V)/c^2]^{-1}\boldsymbol{\sigma}^P\cdot\hat{\boldsymbol{p}}\,\phi^L_{vi}, \tag{4.5}$$

where ϕ^L_{vi} and ϕ^S_{vi} are component functions, ϵ is the energy and V is the potential defining the basis function. This result shows that the matrix elements of the kinetic energy operator take the form

$$\langle\phi_{\mathrm{v}i}|\mathscr{H}_{\mathrm{KE}}|\phi_{\mathrm{v}j}\rangle = \langle\phi_{\mathrm{v}i}|(\tfrac{1}{2}\hat{p}^2)+\sum_{n>1} O(c^{-n})\,|\phi_{\mathrm{v}j}\rangle. \tag{4.6}$$

This result is not computationally tractible because the relativistic corrections $[\Sigma_{n>1}O(c^{-n})]$ contain singular terms although their sum is finite (Pyper 1980*a*; Ketley & Moss 1983). However, equation (4.6) does show that RIP calculations with basis sets satisfying (4.5) will correctly reduce to the corresponding non-relativistic calculations in the limit of large c. This circumvents the difficulties arising from the underestimation of the kinetic energy, even in the large c limit, in relativistic calculations which use conventional basis sets (Mark & Schwartz 1982; Kutzelnigg 1984). The third advantage of the RIP program is that basis superposition errors (Ostlund & Merrifield 1976) are completely absent for the usual choice of basis, containing the occupied Dirac–Fock atomic orbitals of the isolated atoms.

5. COMPUTATIONAL METHODS

(*a*) *One-centre integrals*

The radial parts ($P_A(r_\mu)$ and $Q_A(r_\mu)$) of the central field orbitals (2.3) are computed numerically by the Oxford Dirac–Fock program (Grant *et al.* 1980), which tabulates these functions at a finite number of points equally spaced on a logarithmic grid of step-size h. Thus these functions are tabulated for integral values of the parameter t, defined by

$$r = r_0\,\mathrm{e}^{ht}, \tag{5.1}$$

where r_0 is the first value of r at which $P_A(r)$ and $Q_A(r)$ are computed. These quantities are less than 10^{-9} at the largest value of t considered, where, moreover, they are decreasing exponentially, thus ensuring that larger values of t make a negligible contribution to molecular integrals. The contributions to one-centre integrals from spatial regions between $r = 0$ and r_0 are evaluated by taking the integrand to vary as Ar^q, with the constants A and q determined by the first two defined values of the integrand. Integrals of the type

$$\int_0^\infty F(r)\,\mathrm{d}r = h\int_{-\infty}^\infty r\,F(r)\,\mathrm{d}t \tag{5.2}$$

arise in the final stage of the computation of all one-centre integrals. These quantities are evaluated to high accuracy as in the Oxford Dirac–Fock program (Grant *et al.* 1980), by using Simpson's rule in t space.

The first stage in the evaluation of both one-centre and two-centre kinetic energy integrals requires the computation of the quantities

$$\mathscr{H}_{\mathrm{KE}}|u_{\mu,\,a}\,\kappa_a\,m_a\rangle = (c/r_\mu)\begin{pmatrix}[\kappa_A\,Q_A(r_\mu)/r_\mu-\mathrm{d}Q_A(r_\mu)/\mathrm{d}r_\mu]\,\chi_{k_A,\,m_a}(\Omega_\mu)\\ i[\kappa_A\,P_A(r_\mu)/r_\mu+\mathrm{d}P_A(r_\mu)/\mathrm{d}r_\mu-2cQ_A(r_\mu)]\,\chi_{-k_A,\,m_a}(\Omega_\mu)\end{pmatrix}, \tag{5.3}$$

where Ω_μ denotes the arguments θ_μ and ϕ_μ of the $\chi_{\kappa,\, m}$ function. The necessary first derivatives are calculated by using the six-point scheme of Hartree (1952).

Both one-centre and two-centre electron–electron repulsion integrals are evaluated by using first the expansion (Eyring *et al.* 1944)

$$r_{12}^{-1} = \sum_{L=0}^{\infty} \sum_{M=-L}^{L} (r_<^L/r_>^{L+1})\, C^*_{L,\, M}(\Omega_1) C_{L,\, M}(\Omega_2), \tag{5.4}$$

where $C_{L,\, M}(\Omega)$ is a modified spherical harmonic (Brink & Satchler 1968), while $r_<$ and $r_>$ are the lesser and greater respectively of r_1 and r_2. The calculation of one-centre integrals

$$\langle u_a\, \kappa_a\, m_a\, u_b\, \kappa_b\, m_b | r_{12}^{-1} | u_c\, \kappa_c\, m_c\, u_d\, \kappa_d\, m_d \rangle$$

over the central field orbitals (2.3) is reduced to purely radial integrations by using the angular momentum techniques from the Oxford Dirac–Fock program (Grant *et al.* 1980). The electrostatic potential generated by the charge density $[u_b\, \kappa_b\, m_b(\boldsymbol{r}_2)]^\dagger\, [u_d\, \kappa_d\, m_d(\boldsymbol{r}_2)]$ is given through (5.4) by

$$\langle u_b\, \kappa_b\, m_b | r_{12}^{-1} \,|\, u_d\, \kappa_d\, m_d \rangle = \sum_L V_L(r_1)\, Y_{L,\, m_d - m_b}(\Omega_1), \tag{5.5}$$

with the radial function $V_L(r_1)$ given by

$$V_L(r_1) = (4\pi/2L+1)^{\frac{1}{2}} \left[\int_0^\infty (r_<^L/r_>^{L+1})\, r_2^2\, D^{bd}_{\mathrm{rad}}(r_2)\, \mathrm{d}r_2 \right] \times \int \{ [\chi_{\kappa_b,\, m_b}(\Omega_2)]^\dagger\, C^*_{L,\, m_d - m_b}(\Omega_2)\, [\chi_{\kappa_d,\, m_d}(\Omega_2)]\, \mathrm{d}\Omega_2 \}. \tag{5.6}$$

The spin and angular integrals

$$\int [\chi_{\kappa_b,\, m_b}(\Omega_2)]^+\, C^*_{L,\, M}(\Omega_2)\, [\chi_{\kappa_d,\, m_d}(\Omega_2)]\, \mathrm{d}\Omega_2 = \int [\chi_{-\kappa_b,\, m_b}(\Omega_2)]^+\, C^*_{L,\, M}(\Omega_2)\, [\chi_{-\kappa_d,\, m_d}(\Omega_2)]\, \mathrm{d}\Omega_2 \tag{5.7}$$

are evaluated analytically by using standard angular momentum techniques, the equality (5.7) permitting the complete separation of radial and angular variables in (5.6). The quantity $D^{bd}_{\mathrm{rad}}(r_2)$ in (5.6) is the radial portion of the charge density distribution of electron 2, and is defined by

$$D^{bd}_{\mathrm{rad}}(r_2) = r_2^{-2}\, [P_B(r_2)\, P_D(r_2) + Q_B(r_2)\, Q_D(r_2)]. \tag{5.8}$$

The radial integration in (5.6) defines a $Y_L(r)$ function whose numerical evaluation by solving a pair of differential equations is described by Hartree (1955) and Grant (1970). The final step in the calculation of both one-centre and (via equation (5.40)) some contributions to the two-centre integrals, is to evaluate quantities of the type

$$\int V_L(r_1)\, D^{ac}_{\mathrm{rad}}(r_1)\, Y_{L,\, m_d - m_b}(\Omega_1)\, Y_{L',\, M'}(\Omega_1)\, \mathrm{d}\boldsymbol{r}_1 = \delta_{L,\, L'}\, \delta_{m_d - m_b,\, -M'} \int_0^\infty r_1^2\, V_L(r_1)\, D^{ac}_{\mathrm{rad}}(\mathrm{r}_1)\, \mathrm{d}r_1. \tag{5.9}$$

Here $Y_{L',\, M'}(\Omega_1)$ is a spherical harmonic generated from the charge density $[u_a(r_1)]^\dagger\, [u_c(r_1)]$ after performing the spinor multiplications and using (5.26) to handle products of spherical harmonics.

(*b*) *Two-centre, one-electron and direct inner-core potential integrals*

Overlap integrals between two central field orbitals (2.3) located on different centres can be expressed as a sum of four integrals of the type defined by (5.41) below. Two-centre kinetic energy integrals also take this form with $F_b(r_2)$ already known from (5.3). Integrals between two atomic orbitals on different centres over the electrostatic potential (3.43), generated by the nuclei plus inner-core electrons, take the form (5.41) with $F_b(r_2)$ given by the product of $\hat{V}_{2\mathrm{core}}(r_2)$ with the radial part of the orbital located on centre 2. The methods used to compute these integrals are described in §5*d*.

The two-centre nuclear attraction plus inner-core repulsion integrals with the potential (3.43) on a different centre from the common one of the two orbitals involve integrals of the type

$$\int r_1^{-1} F_a(r_1)\, Y^*_{l_a,\, m_a}(\Omega_1)\, r_2^{-1} F_b(r_2)\, Y_{l_b,\, m_b}(\Omega_1)\, \mathrm{d}\boldsymbol{r}_1. \tag{5.10}$$

These are evaluated by the procedure used for (5.9), except that the associated Legendre polynomial $\Theta_{l_b,\, m_b}(\theta_2)$ is replaced by $\Theta_{l_b,\, m_b}(\theta_1)$ throughout §5*d*.

(*c*) *Electron repulsion integrals between orthonormal orbitals*

(i) *Introduction*

Two-centre, two-electron integrals take the general form:

$$I = \langle \phi_a\, m_a | \langle \phi_b\, m_b | r_{12}^{-1} | \phi_c\, m_c \rangle\, | \phi_d\, m_d \rangle, \tag{5.11}$$

where $a = d, b = c$ for a 'coulomb' integral and $a = c, b = d$ for an 'exchange' integral.

The two-centre potential $\langle \phi_b\, m_b | r_{12}^{-1} | \phi_c\, m_c \rangle$ is evaluated by first expressing the orthonormal orbitals in terms of their one-centre compound functions

$$|\phi_a\, m_a\rangle = \sum_{\kappa} \sum_{\mu} |\Omega_{a\mu\, \kappa m_a}\rangle, \tag{5.12}$$

so that the potential becomes

$$\langle \phi_b\, m_b | r_{12}^{-1} | \phi_c\, m_c \rangle = \sum_{\kappa} \sum_{\kappa'} \sum_{\mu} \sum_{\mu'} \langle \Omega_{b\mu\, \kappa m_b} | r_{12}^{-1} | \Omega_{c\mu'\, \kappa' m_c} \rangle. \tag{5.13}$$

The one-centre terms ($\mu = \mu'$) could be calculated by using the one-centre methods shown in the previous section, but it is more convenient to calculate them at the same time as the two-centre terms. However, the two-centre methods ($\mu \neq \mu'$) are more complicated.

(ii) *Second-centre expansion*

In non-relativistic calculations which use Slater or Gaussian basis functions, multi-centre integrals such as (5.11) are evaluated either by using the special properties of the basis functions or by moving functions from one centre to another (expressing them as the sum of a series of functions on the new centre: see, for example, Barnett & Coulson 1951). The numerical wavefunctions used in this work clearly have no special properties, so a method which involves moving functions has to be used.

The basic problem is to express the spinor $|\Omega_{a1\kappa m_a}\rangle$ in terms of functions on centre 2. The method developed here requires that each of the spinor's four components be expanded separately on the second centre. This means that the final expression is not an expansion in terms of atomic spinors on the second centre satisfying the usual equivalence conditions, but simply a group of four separate expansions. Consequently, the calculations of the two-centre terms in (5.13) is considerably less elegant than the calculation of the one-centre terms.

Each component of the spinor is a function of the form $r_1^{-1} P(r_1)\, Y_{l_m}(\boldsymbol{r}_1)$ and it is required to express this in terms of similar functions on centre 2. The coordinate system is shown in figure 1. The radial and angular functions can be 'moved' separately, because the spherical harmonics can be expressed in terms of harmonics on the second centre analytically, by means of the solid harmonic addition theorem. The regular solid harmonics $R_l^m(\boldsymbol{r})$ are defined by Caola (1978):

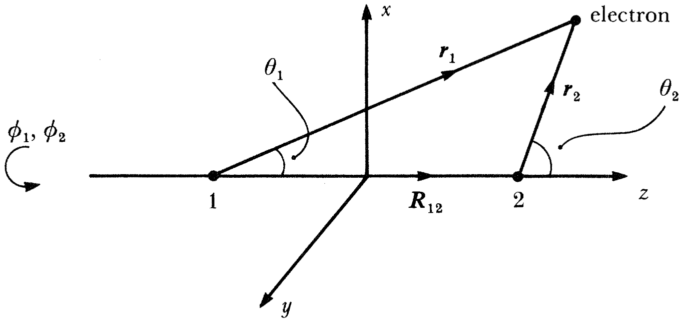

FIGURE 1. The coordinate system.

$$R_l^m(\boldsymbol{r}) = r^l(-1)^m \left[\frac{(l+m)!}{(l-m)!}\right]^{\frac{1}{2}} \left(\frac{4\pi}{2l+1}\right)^{\frac{1}{2}} Y_{l,m}(\boldsymbol{r})$$
$$= r^l P_l^m(\cos\theta)\, \mathrm{e}^{\mathrm{i}m\phi}. \tag{5.14}$$

Given that $\boldsymbol{r}_b = \boldsymbol{r}_a - \boldsymbol{r}_{ab}$, the solid harmonic addition theorem states that (Caola 1978)

$$R_l^m(\boldsymbol{r}_b) = \sum_{l'} \sum_{m'} (-1)^{l-l'} \binom{l+m}{l'+m'} R_{l'}^{m'}(\boldsymbol{r}_a)\, R_{l-l'}^{m-m'}(\boldsymbol{r}_{ab}). \tag{5.15}$$

In the coordinate system shown in figure 1,

$$\boldsymbol{r}_1 = \boldsymbol{r}_2 + \boldsymbol{R}_{12}$$
$$= \boldsymbol{r}_2 - \boldsymbol{R}_{21}, \tag{5.16}$$

and it is clear that the spherical coordinate θ for $\boldsymbol{R}_{12}$ is equal to π (by using coordinates relative to centre 2), so that

$$R_l^m(\boldsymbol{R}_{21}) = R_{21}^l\, P_l^m(\cos\pi)\, \mathrm{e}^{\mathrm{i}m\phi}$$
$$= R_{21}^l (-1)^l\, \delta_{m0}. \tag{5.17}$$

Combining (5.15), (5.16) and (5.17) yields

$$R_l^m(\boldsymbol{r}_1) = \sum_{l'} \sum_{m'} (-1)^{l-l'} \binom{l+m}{l'+m'} R_{l'}^{m'}(\boldsymbol{r}_2)\, R_{21}^{l-l'} (-1)^{l-l'}\, \delta_{(m-m')0}$$
$$= \sum_{l'} \binom{l+m}{l'+m} R_{l'}^{m}(\boldsymbol{r}_2)\, R_{21}^{l-l'}, \tag{5.18}$$

so that

$$r_1^l\, Y_{l,\,m}(\boldsymbol{r}_1) = \left[\frac{(l-m)!}{(l+m)!}\right]^{\frac{1}{2}}(2l+1)^{\frac{1}{2}} \sum_{l'=|m|}^{l'=l}\left\{\left[\frac{(l'+m)!}{(l'-m)!}\right]^{\frac{1}{2}}\frac{1}{(2l'+1)^{\frac{1}{2}}}\binom{l+m}{l'+m} r_2^{l'} R_{21}^{l-l'}\, Y_{l',\,m}(\boldsymbol{r}_2)\right\}, \tag{5.19}$$

which completes the expansion.

This spherical harmonic expansion leaves a term $r_1^{-l-1}P(r_1)$ to be expressed in terms of functions on centre 2. This term is expanded as a series of spherical harmonics; each multiplied by a radial function $P'_{sm}(r_2)$:

$$\frac{1}{r_1^{l+1}}P(r_1) = \sum_{s=0}^{\infty} P'_{sm}(r_2)\, Y_{s,\,m}(\boldsymbol{r}_2). \tag{5.20}$$

The functions $P'_{sm}(r_2)$ are evaluated by using the orthogonality properties of the spherical harmonics:

$$\int \frac{P(r_1)}{r_1^{l+1}}\, Y^*_{s',\,m'}(\boldsymbol{r}_2)\,\mathrm{d}\Omega = \int\left[\sum_{s=0}^{\infty} P'_{sm}(r_2)\, Y_{s,\,m}(\boldsymbol{r}_2)\right] Y^*_{s',\,m'}(\boldsymbol{r}_2)\,\mathrm{d}\Omega$$

$$= \sum_{s=0}^{\infty} P'_{sm}(r_2)\,\delta_{ss'}\,\delta_{mm'}. \tag{5.21}$$

It is clear that because $P(r_1)$ has cylindrical symmetry about the z axis, and hence is independent of the coordinate ϕ_2, that the left side in (5.21) is zero for $m' \neq 0$. The m label on $P'_{sm}(r_2)$ is therefore superfluous, and will be omitted from now on. This leaves

$$P'_s(r_2) = \int \frac{P(r_1)}{r_1^{l+1}}\, Y^*_{s,\,0}(\boldsymbol{r}_2)\,\mathrm{d}\Omega. \tag{5.22}$$

Noting that

$$Y^*_{s,\,0}(\boldsymbol{r}_2) = (1/\surd(2\pi))\,\Theta_{s,\,0}(\theta_2), \tag{5.23}$$

where $\mathrm{d}\Omega = \sin\theta_2\,\mathrm{d}\theta_2\,\mathrm{d}\phi_2$ and $\Theta_{s,\,0}(\theta_2)$ is an associated Legendre polynomial, gives:

$$P'_s(\boldsymbol{r}_2) = \surd(2\pi)\int_0^{\pi}\frac{P(r_1)}{r_1^{l+1}}\,\Theta_{s,\,0}(\theta_2)\sin\theta_2\,\mathrm{d}\theta_2. \tag{5.24}$$

Combining the separate angular and radial expressions (5.19) and (5.20) yields:

$$\frac{1}{r_1}P(r_1)\, Y_{l,\,m}(\boldsymbol{r}_1) = \left[\frac{(l-m)!}{(l+m)!}\right]^{\frac{1}{2}}(2l+1)^{\frac{1}{2}}\sum_{l'=|m|}^{l'=l}\left\{\left[\frac{(l'+m)!}{(l'-m)!}\right]^{\frac{1}{2}}\right.$$

$$\left.\times\frac{1}{(2l'+1)^{\frac{1}{2}}}\binom{l+m}{l'+m} r_2^{l'} R_{21}^{l-l'}\, Y_{l',\,m}(\boldsymbol{r}_2)\right\}\sum_{s=0}^{\infty} P'_s(r_2)\, Y_{s,\,0}(\boldsymbol{r}_2). \tag{5.25}$$

The product of spherical harmonics can be expressed as a sum of harmonics by using the formula (Brink & Satchler 1968)

$$Y_{s,\,0}\, Y_{l',\,m} = \frac{(2s+1)^{\frac{1}{2}}(2l'+1)^{\frac{1}{2}}}{2\pi^{\frac{1}{2}}}\sum_k\left[Y_{k,\,m}(2k+1)^{\frac{1}{2}}(-1)^m\begin{pmatrix} s & l' & k\\ 0 & m & -m\end{pmatrix}\begin{pmatrix} s & l' & k\\ 0 & 0 & 0\end{pmatrix}\right], \tag{5.26}$$

where $|s-l'| \leqslant k \leqslant s+l'$ and $k \geqslant m$ and $k+l'+s$ is even.

Including this in (5.25) and re-ordering the summation yields the final result

$$\frac{1}{r_1}P(r_1)\,Y_{l,\,m}(\boldsymbol{r}_1) = \sum_{k=|m|}^{\infty}\left\{\sum_{l'=|m|}^{l}\;\sum_{s=|l'-k|}^{l'+k} Y_{k,\,m}(\boldsymbol{r}_2)\,r_2^{l'}\,R_{21}^{l-l'}\right.$$
$$\times P'_s(r_2)\left[\frac{(2k+1)^{\frac{1}{2}}\,(-1)^m}{2\pi^{\frac{1}{2}}}\left(\frac{(l-m)!}{(l'+m)!}\,\frac{(l+m)!}{(l'-m)!}\right)^{\frac{1}{2}}\right.$$
$$\left.\left.\times\frac{(2l+1)^{\frac{1}{2}}\,(2s+1)^{\frac{1}{2}}}{(l-l')!}\begin{pmatrix} s & l' & k\\ 0 & m & -m\end{pmatrix}\begin{pmatrix} s & l' & k\\ 0 & 0 & 0\end{pmatrix}\right]\right\}, \tag{5.27}$$

where the binomial coefficient appearing in (5.25) has been expressed explicitly in terms of factorials. The summations over s and k have been interchanged to show how the expansion is performed in practice: the functions $P'_s(r_2)$ are first evaluated by using (5.24) and are then combined to yield new functions $P''_{klm}(r_2)$:

$$P''_{klm}(r_2) = \sum_{l'=|m|}^{l}\;\sum_{s=|l'-k|}^{l'+k} r_2^{l'}\,R_{21}^{l-l'}\,P'_s(r_2)\left[\frac{(2k+1)^{\frac{1}{2}}\,(-1)^m}{2\pi^{\frac{1}{2}}}\right.$$
$$\left.\times\left(\frac{(l-m)!}{(l'+m)!}\,\frac{(l+m)!}{(l'-m)!}\right)^{\frac{1}{2}}\frac{(2l+1)^{\frac{1}{2}}\,(2s+1)^{\frac{1}{2}}}{(l-l')!}\begin{pmatrix} s & l' & k\\ 0 & m & -m\end{pmatrix}\begin{pmatrix} s & l' & k\\ 0 & 0 & 0\end{pmatrix}\right], \tag{5.28}$$

so that:
$$\frac{1}{r_1}P(r_1)\,Y_{l,\,m}(\boldsymbol{r}_1) = \sum_{k=m}^{\infty} P''_{klm}(r_2)\,Y_{k,\,m}(\boldsymbol{r}_2). \tag{5.29}$$

This means that a function on one centre can be expanded in terms of a set of similar functions on another centre, so that it is possible to reduce the two-centre terms appearing in (5.12) to purely one-centre terms.

Though the summation is infinite, in practice it converges fairly rapidly providing $P(r_1)$ is not too localized.

(iii) *Density and potential function expansions*

It was mentioned in the previous section that because the orbital radial functions are held as a table of discrete values, it is more efficient computationally to add the radial functions together, wherever possible, and then integrate over the sum, rather than sum the result of many separate integrations over the original orbitals. Therefore, instead of evaluating (5.13) by using the result derived in §5*c* (ii) for the two-centre terms, the summation is moved inside the integration to form a combined density function, which is then integrated to obtain the potential.

Each one-centre orbital, $|\Omega_{\mu\kappa m}\rangle$, in equation (5.13) is a four-component function:

$$|\Omega_{\mu\kappa m}\rangle = \frac{1}{r_\mu}\begin{pmatrix} P_m(r_\mu)\,\langle l\tfrac{1}{2}m-\tfrac{1}{2}\tfrac{1}{2}\,|jm\rangle\,Y_{l,\,m-\frac{1}{2}}\\ P_m(r_\mu)\,\langle l\tfrac{1}{2}m+\tfrac{1}{2}-\tfrac{1}{2}\,|jm\rangle\,Y_{l,\,m+\frac{1}{2}}\\ iQ_m(r_\mu)\,\langle l+a\tfrac{1}{2}m-\tfrac{1}{2}\tfrac{1}{2}\,|jm\rangle\,Y_{l+a,\,m-\frac{1}{2}}\\ iQ_m(r_\mu)\,\langle l+a\tfrac{1}{2}m+\tfrac{1}{2}-\tfrac{1}{2}\,|jm\rangle\,Y_{l+a,\,m+\frac{1}{2}}\end{pmatrix}, \tag{5.30}$$

where $j = l+\frac{1}{2}a$ and $a = +1$ for $k < 0$ and $a = -1$ for $k > 0$. If $|\Omega_{\mu\kappa m}\rangle$ is moved to the second centre by using (5.29), it is expressed as

$$|\Omega_{\mu\kappa m}\rangle = \begin{pmatrix} \sum\limits_{s=|m-\frac{1}{2}|}^{\infty} P''_{slm-\frac{1}{2}}(r_{\mu'})\, Y_{sm-\frac{1}{2}}(\boldsymbol{r}_{\mu'}) \\ \sum\limits_{s=|m+\frac{1}{2}|}^{\infty} P''_{slm+\frac{1}{2}}(r_{\mu'})\, Y_{sm+\frac{1}{2}}(\boldsymbol{r}_{\mu'}) \\ \mathrm{i}\sum\limits_{s=|m-\frac{1}{2}|}^{\infty} Q''_{sl+am-\frac{1}{2}}(r_{\mu'})\, Y_{sm-\frac{1}{2}}(\boldsymbol{r}_{\mu'}) \\ \mathrm{i}\sum\limits_{s=|m+\frac{1}{2}|}^{\infty} Q''_{sl+am+\frac{1}{2}}(r_{\mu'})\, Y_{sm+\frac{1}{2}}(\boldsymbol{r}_{\mu'}) \end{pmatrix}. \tag{5.31}$$

The density D^{ab} is now defined as

$$D^{ab} = \sum_{\kappa}\sum_{\kappa'}\sum_{\mu}\sum_{\mu'} \Omega^{*}_{a\mu\kappa m_a}\,\Omega_{b\mu'\kappa' m_b}. \tag{5.32}$$

This is evaluated by considering each component in turn. Then, for each one-centre term ($\mu = \mu'$), one integrates over the spin function (which yields unity), multiplies the radial functions together and uses the spherical harmonic product rule to express the angular function as a sum of individual spherical harmonics. Any coefficients are combined with the new radial function. For example:

$$\begin{aligned} &\frac{1}{r_\mu} P_a(r_\mu)\,\langle l_a \tfrac{1}{2} m_a - \tfrac{1}{2}\tfrac{1}{2}\,|\, jm\rangle\, Y^{*}_{l_a,\, m_a-\frac{1}{2}}(\boldsymbol{r}_\mu)\, \frac{1}{r_\mu} P_b(r_\mu)\,\langle l_b \tfrac{1}{2} m_b - \tfrac{1}{2}\tfrac{1}{2}\,|\, jm\rangle\, Y_{l_b,\, m_b-\frac{1}{2}}(\boldsymbol{r}_\mu) \\ &\qquad = \sum_{l=|l_a-l_b|}^{l_a+l_b} D_l(r_\mu)\, Y_{l,\, m_b-m_a}(\boldsymbol{r}_\mu), \end{aligned} \tag{5.33}$$

where:

$$D_l(r_\mu) = \frac{P_a(r_\mu)\,P_b(r_\mu)}{r_\mu^2}\, \frac{(2l_a+1)^{\frac{1}{2}}\,(2l_b+1)^{\frac{1}{2}}}{(2l+1)} \begin{pmatrix} l_a & l_b & l \\ -m_a & m_b & m_a-m_b \end{pmatrix} \begin{pmatrix} l_a & l_b & l \\ 0 & 0 & 0 \end{pmatrix}. \tag{5.34}$$

The results (5.33) for each term are combined into two separate series (one for each centre) by summing all of the radial functions associated with a unique spherical harmonic.

The two-centre terms are dealt with in a similar fashion. One component function in each product

$$(1/r_\mu)\, P_a(r_\mu)\, Y_{l_a,\, m_a-\frac{1}{2}}(\boldsymbol{r}_\mu)\,(1/r_{\mu'})\, P_b(r_{\mu'})\, Y_{l_b,\, m_b-\frac{1}{2}}(\boldsymbol{r}_{\mu'}) \tag{5.35}$$

is chosen to be expressed on the second centre (the criteria behind this choice are described in §5*d*). This gives an infinite sum of one-centre terms. For example, if function a is chosen to be moved to centre μ', then the term (5.35) becomes

$$\sum_{s=|m_a-\frac{1}{2}|}^{\infty} P''_{sl_a m_a-\frac{1}{2}}(r_{\mu'})\, Y_{s,\, m_a-\frac{1}{2}}(\boldsymbol{r}_{\mu'})\, \frac{1}{r_{\mu'}} P_b(r_{\mu'})\, Y_{l_b,\, m_b-\frac{1}{2}}(\boldsymbol{r}_{\mu'}), \tag{5.36}$$

which yields a similar result to (5.33), except that the summation involves an infinite series of spherical harmonics and $1/r_\mu$ is omitted from (5.34).

Each two-centre term is added to the appropriate one-centre series formed from the one-centre terms. Each of the four components yields a separate pair of series. However, all of the spherical harmonics in all the series have the same m index value ($m_b - m_a$), so that the four individual series on each centre can be combined into a single series. The resulting density function, D^{ab}, therefore has the form

$$D^{ab} = \sum_{\mu} \sum_{l=|m_b-m_a|}^{\infty} D^{ab}_{l\mu}\, Y_{l,\, m_b-m_a}(\boldsymbol{r}_{\mu}), \tag{5.37}$$

where $D^{ab}_{l\mu}$ is the radial function associated with the spherical harmonics $Y_{l,\, m_b-m_a}$ on centre μ.

The potential function (5.13) can now be calculated from the density:

$$\langle \phi_b\, m_b | r_{12}^{-1} | \phi_c\, m_c \rangle = \sum_{\mu} \sum_{l=|m_c-m_b|}^{\infty} \int \frac{1}{r_{12}} D^{bc}_{l\mu}(r_{\mu})\, Y_{l,\, m_c-m_b}(\boldsymbol{r}_{\mu})\, \mathrm{d}\Omega. \tag{5.38}$$

Each term in the right side of (5.38) is evaluated by using the one-centre methods described in §5*a* (expression (5.4) for r_{12}^{-1} is used and the one-centre potential integrals (5.6) computed numerically). The terms combine to give a new series for the potential,

$$\langle \phi_b\, m_b | r_{12}^{-1} | \phi_c\, m_c \rangle = \sum_{\mu} \sum_{l=|m_c-m_b|}^{\infty} V^{bc}_{l\mu}(r_{\mu})\, Y_{l,\, m_c-m_b}(\boldsymbol{r}_{\mu}), \tag{5.39}$$

where $V^{bc}_{l\mu}(r_{\mu})$ is the radial function formed by summing all of the radial potentials associated with the same spherical harmonic.

The general repulsion integral is now simply given by:

$$\begin{aligned} \langle \phi_a\, m_a | \langle \phi_b\, m_b | r_{12}^{-1} | \phi_c\, m_c \rangle\, | \phi_d\, m_d \rangle &= \int D^{ad} \sum_{\mu} \sum_{l=|m_c-m_b|}^{\infty} V^{bc}_{l\mu}(r\mu)\, Y_{l,\, m_c-m_b}(\boldsymbol{r}_{\mu})\, \mathrm{d}\Omega \\ &= \sum_{\mu} \sum_{\mu'} \sum_{l=|m_d-m_a|}^{\infty} \sum_{l'=|m_c-m_b|}^{\infty} \int D^{ad}_{l\mu}(r_{\mu})\, Y_{l,\, m_d-m_a}(\boldsymbol{r}_{\mu})\, V^{bc}_{l'\mu'}(r_{\mu'})\, Y_{l',\, m_c-m_b}(\boldsymbol{r}_{\mu'})\, \mathrm{d}\Omega. \end{aligned} \tag{5.40}$$

The one-centre terms in (5.40) are calculated by using the numerical methods described in §5*a*. The two-centre terms are calculated by using methods described in §5*d*.

(*d*) *Numerical methods for two-centre integrals*

Unlike one-centre integrals, it is not possible to simplify two-centre integrals directly by using angular momentum techniques. Each component has to be integrated separately, so that for the overlap integral, four separate integrations are required. Each integration takes the form

$$I = \int \frac{F_a(r_1)}{r_1}\, Y^{*}_{l_a,\, m_a}(\boldsymbol{r}_1)\, \frac{F_b(r_2)}{r_2}\, Y_{l_b,\, m_b}(\boldsymbol{r}_2)\, \mathrm{d}\tau, \tag{5.41}$$

where F_a and $Y_{l_a,\, m_a}$ are on centre 1 and F_b and $Y_{l_b,\, m_b}$ are on centre 2; $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ refer to the position of the electron relative to centres 1 and 2 respectively, as shown in figure 1. Integrals with the same form as (5.41) also occur in the evaluation of electron repulsion integrals over orthonormal orbitals (5.40).

The following method for the numerical evaluation of (5.41) was adopted after considerable experiment. It has been found to be accurate, efficient and very reliable.

By first integrating analytically over coordinate ϕ, this integral becomes

$$I = 2\pi \int_0^{\infty} \int_{|R-r_2|}^{R+r_2} \frac{F_a(r_1)}{r_1}\, \Theta_{l_a,\, m_a}(\theta_1)\, \frac{F_b(r_2)}{r_2}\, \Theta_{l_b,\, m_b}(\theta_2)\, \frac{r_1 r_2}{R}\, \mathrm{d}r_1\, \mathrm{d}r_2\, \delta_{m_a m_b}, \tag{5.42}$$

where the Θs are associated Legendre polynomials, and $r_1 r_2/R$ is the Jacobian for the coordinate system, based on r_1 and r_2 and ϕ. The logarithmic coordinates on which r_1 and r_2 are based are

$$r_1 = r_0\,\mathrm{e}^{ht_1}; \quad r_2 = r_0\,\mathrm{e}^{ht_2}, \tag{5.43}$$

and the integral (5.42) becomes:

$$I = \int_{-\infty}^{\infty}\int_{t_1^-}^{t_1^+} F_a(r_1)\,\Theta_{l_a,\,m_a}(\theta_1)\,F_b(r_2)\,\Theta_{l_b,\,m_b}\,\frac{r_1 r_2}{R}\,\mathrm{d}t_1\,\mathrm{d}t_2\,\delta_{m_a\,m_b}, \tag{5.44}$$

where
$$t_1^+ = 1/h\,\lg\,[(R+r_2)/r_0], \quad t_1^- = 1/h\,\lg\,|[(R-r_2)/r_0]|. \tag{5.45}$$

Unfortunately, the integral (5.44) is not symmetric in the coordinates t_1 and t_2: the integration is on half-circles about centre 2 as t_1 goes from $-\infty$ to $+\infty$. The use of this form as a basis for numerical integration gives unreliable results because the integration is very coarse near centre 1, from where a large contribution to the integral is expected to come. The problem is avoided by dividing the integration range into several symmetric areas.

$$I = \int_{-\infty}^{t_c}\int_{t_1^-}^{t_1^+} X\,\mathrm{d}t_1\,\mathrm{d}t_2 + \int_{-\infty}^{t_c}\int_{t_2^-}^{t_2^+} X\,\mathrm{d}t_1\,\mathrm{d}t_2 + \int_{t_c}^{\infty}\int_{t_2}^{t_1^+} X\,\mathrm{d}t_1\,\mathrm{d}t_2 + \int_{t_c}^{\infty}\int_{t_1}^{t_2^+} X\,\mathrm{d}t_2\,\mathrm{d}t_1, \tag{5.46}$$

where
$$t_c = 1/h\,\lg\,(R/2r_0),$$
$$t_2^+ = 1/h\,\lg\,[(R+r_1)/r_0], \quad t_2^- = 1/h\,\lg\,|[(R-r_1)/r_0]|$$
$$X = 2\pi\,F_a(r_1)\,\Theta_{l_a,\,m_a}(\theta_1)\,F_b(r_2)\,\Theta_{l_b,\,m_b}(\theta_2). \tag{5.47}$$

In physical terms, one integrates about each centre separately, over the volume extending from the plane $z = 0$ to $z = +\infty$ for centre 1 and over the volume extending from $z = 0$ to $z = -\infty$ for centre 2.

The integrals in (5.46) are calculated with 24 × 24 point Gauss quadrature, with the use of sixth-order Legendre interpolation to obtain the values of F_a and F_b at the quadrature points. The integration range is limited to $0 \leqslant t_1, t_2 < 400$; F_a and F_b are always $< 10^{-9}$ for $t \geqslant 400$, and by omitting the nucleus regions $r_1 < r_0$ and $r_2 < r_0$ negligible errors are obtained.

Because integrals involving numerical relativistic orbitals on more than one centre have not been previously calculated, the integration scheme was tested by calculating integrals over non-relativistic Slater orbitals. Slater orbitals were chosen because they have the same long-range behaviour as relativistic orbitals and because integrals involving them can be evaluated to high precision by using the ALCHEMY molecular integrals program.

The number of points in the Gaussian quadrature was chosen by doing several tests with an increasing number of integration points. In each test, a large number of integrals of the form (5.41), including a wide range of spherical harmonics, were calculated. It was found that with 24 × 24 point Gaussian quadrature, all of the integrals had a precision of better than nine decimal places, so all subsequent calculations were done with this number of integration points.

The expansion of orbitals on a second centre was tested in a similar fashion by calculating exchange integrals involving Slater orbitals, i.e. integrals of the form

$$I = \langle \phi_i\,\phi_j |\, r_{12}^{-1} | \phi_k\,\phi_l \rangle, \tag{5.48}$$

where orbitals ϕ_i and ϕ_j are on centre 1 and orbitals ϕ_k and ϕ_l are on centre 2. For simple individual integrals such as (5.48), it is only necessary to move one function, and all of the test integrals were calculated in this way. However, the method developed in §5*c* requires in general that two orbitals be moved, but the results discussed below will show that the underlying method is sound.

The test calculations showed that it is better to move a diffuse function, rather than a contracted one, because far more terms with high angular momentum quantum values are required to fit a sharply peaked function situated away from the expansion centre. It was found that provided the more diffuse orbital of the pair of orbitals occupied by one electron was moved, an expansion including terms up to $l = 17$ always gave results accurate to at least six decimal places. Integrals involving two contracted orbitals are not in fact a problem, since the overlap between the orbitals is small and the integral correspondingly tiny.

The correctness of the complicated programming of RIP as a whole and the accuracy of the numerical methods were tested by calculating the interaction energy between inert gas atoms, with the use of exact non-relativistic atomic Hartree–Fock wavefunctions. The detailed results are given by Wood & Pyper (1981*c*). Thus, for the neon dimer, the interaction energies agree with those computed by Gilbert & Wahl (1967) from the traditional basis set methods of quantum chemistry, to within 0.0003 a.u., except at the shortest separation, $R = 2.5$ a.u., where the discrepancy is slightly greater. These discrepancies can be ascribed to the deviation of the Gilbert & Wahl basis-set atomic functions from those at the exact non-relativistic Hartree–Fock limit. For example, at $R = 3.5$ a.u., Gilbert & Wahl found an interaction energy of 0.0301 a.u., compared to 0.0303 a.u. found in the present calculations by using the exact non-relativistic Hartree–Fock wavefunctions. However, when this interaction energy was calculated from the present program but inputting the Gilbert & Wahl wavefunctions, this small discrepancy disappeared completely. In this calculation the small components were set to zero, and the matrix elements of the non-relativistic kinetic energy operator were calculated by using the same numerical methods. Although it is not the purpose of this paper to present results of RIP calculations for diatomic molecules, it should be noted that the program has been further tested by using it to compute non-relativistic self-consistent field wavefunctions of near Hartree–Fock quality for first-row hydrides. These calculations, to be reported in detail elsewhere, were performed simply by increasing the value of c used both in the RIP program and in the Oxford Dirac–Fock program used to generate the input atomic wavefunctions.

6. APPLICATION TO IONIC SOLIDS

(*a*) *Method*

The RIP program provides the means for undertaking a non-empirical study of ionic solids containing the heaviest ions. It is shown in the companion paper (Pyper 1986) that it is useful to regard the crystal as being formed from its constituent ions in two stages. In the first stage the isolated free ions are modified to a non-stationary state. In the second stage these modified ions are assembled to form the crystal with the correct structure but with closest cation–anion separation (R) not, in general, equal to the equilibrium value (R_e). The crystal structure parametrized by closest cation–anion separation (R) differs from the equilibrium cubic structure solely by a uniform contraction or expansion of the entire crystal. If all effects arising from electron correlation are neglected, the binding energy ($U^0_L(R)$) per formula unit of crystal CA_m (composed of cations C and anions A, relative to the free ions is given by

$$U^0_L(R) = -M/R + n_{\text{CA}}\, V^0_{s\text{CA}}(R) + \tfrac{1}{2}[n_{\text{CC}}\, V^0_{s\text{CC}}(x_{\text{CC}}\, R) + m\, n_{\text{AA}}\, V^0_{s\text{AA}}(x_{\text{AA}}\, R)] + E^{\text{C}}_{\text{Re}}(R) + m\, E^{\text{A}}_{\text{Re}}(R). \tag{6.1}$$

Here, M is the Madelung constant, n_{ab} is the number of nearest b ions around each a ion and x_{aa} relates the distance ($x_{\text{aa}}\, R$) between the closest pair of ions a to the distance R. The quantity $E^{\text{a}}_{\text{Re}}(R)$ is the rearrangement energy needed to convert a free ion a to the non-stationary state that subsequently minimizes the (negative) binding energy $U^0_L(R)$. Thus the second line of (6.1) is the total energy required in the first of the two stages into which it is useful to decompose the binding energy. The former energy is readily computed by using the Oxford Dirac–Fock program (Grant *et al.* 1980) from the Dirac–Fock wavefunctions of both the free ions and the ions in their non-stationary states. The energy change upon assembling the ions in their non-stationary states to form the crystal is given by the first line of (6.1) if the energy of interaction of each pair of ions, excepting the closest cation–anion, cation–cation and anion–anion pairs, is taken to have the purely coulombic form $q_{\text{a}}\, q_{\text{b}}/(x_{\text{ab}}\, R)$ with q_{a} the charge of ion a. The energy ($V^0_{\text{ab}}(x_{\text{ab}}\, R)$) of the pair of ions a and b, separated by a distance $x_{\text{ab}}\, R$ relative to that of the infinitely separated pair of ions in their non-stationary states, can be computed by using the RIP program, being the quantity $\Delta E^{\text{int}}_{\text{core}}$ (equation (3.31)). It is convenient to decompose this energy into a point-coulombic plus a short-range term $V^0_{\text{sab}}(x_{\text{ab}}\, R)$, appearing in (6.1) through

$$V^0_{\text{ab}}(x_{\text{ab}}\, R) = V^0_{\text{sab}}(x_{\text{ab}}\, R) + q_{\text{a}}\, q_{\text{b}}/(x_{\text{ab}}\, R). \tag{6.2}$$

The contribution to the crystal binding energy which arises from electron correlation can be decomposed (Pyper 1986) into a sum of short-range corrections to the potentials $V^0_{\text{sab}}(x_{\text{ab}}\, R)$, plus a long-range term ($U^{\text{un}}_{\text{disp}}(R)$) composed of the dispersive (London) attractions between the ions. The binding energy ($U_{\text{L}}(R)$) including correlation is given by

$$U_{\text{L}}(R) = U^0_{\text{L}}(R) + n_{\text{CA}}\, V^{\text{corr}}_{\text{sCA}}(R) + \tfrac{1}{2}[n_{\text{CC}}\, V^{\text{corr}}_{\text{sCC}}(x_{\text{CC}}\, R) + m\, n_{\text{AA}}\, V^{\text{corr}}_{\text{sAA}}(x_{\text{AA}}\, R)] + U^{\text{un}}_{\text{disp}}(R). \tag{6.3}$$

Here $V^{\text{corr}}_{\text{sab}}(x_{\text{ab}}\, R)$ is the correction to $V^0_{\text{sab}}(R)$ arising from that part of the electron correlation that is non-zero solely by virtue of the overlap between wavefunctions of the pairs of ions a and b. These terms are negligible except for the closest cation–anion, cation–cation and anion–anion pairs for which they can be calculated from the electron densities of the ions by using density functional theory based on the uniform electron gas (Gordon & Kim 1972).

The crystal dispersion energy ($U^{\text{un}}_{\text{disp}}(R)$) is taken to be the sum of the dipole–dipole and dipole–quadrupole dispersive attractions between all the pairs of ions in the crystal (Pyper 1986). It is given by

$$U^{\text{un}}_{\text{disp}}(R) = -\sum_{n=6,\,8} \{S_n(CA)\, C_n(CA) + \tfrac{1}{2}[S_n(CC)\, C_n(CC) + m\, S_n(AA)\, C_n(AA)]\}\, R^{-n}, \tag{6.4}$$

where $C_6(XY)$ and $C_8(XY)$ are the dipole–dipole and dipole–quadrupole dispersion coefficients, yielding the respective attractions between a pair of ions X and Y as $-C_6(XY)/R^6_{XY}$ and $-C_8(XY)/R^8_{XY}$. The derivation of these coefficients is described in the companion paper (Pyper 1986). Each quantity $S_n(XY)$ is a purely geometrical constant reported elsewhere (Pyper 1986), which results from the dispersive attractions dependent on $C_n(XY)$ summed over all the ions in the crystal. The form (6.4) neglects the damping of the dispersion energy arising from overlap of the ion wavefunctions. Overlap invalidates the multipole expansion required to derive the standard long-range form (6.4) for the dispersion energy (Kreek & Meath 1969; Jacobi & Csanak 1975).

The closest cation–anion separation (R_e), the lattice energy ($-U_L(R_e)$) and bulk compressibility (B) can be predicted from the function $U_L(R)$. The compressibility, defined by

$$B = (V\,\mathrm{d}^2U_L(R)/\mathrm{d}V^2)_{R=R_e},$$

with V the molecular volume, is given by

$$B = (9\,k_v\,R_e)^{-1}\,(\mathrm{d}^2U_L(R)/\mathrm{d}R^2)_{R=R_e}, \tag{6.5}$$

where k_v is the constant relating V to R through $V = k_v\,R^3$). Each value of B was derived by using the R_e value predicted from the same calculation.

(b) *Results*

(i) *Introductory*

For five ionic crystals, this subsection presents the lattice energies, closest equilibrium cation–anion separations (R_e) and compressibilities predicted from (6.1) or (6.3) by using the RIP program to calculate exactly the uncorrelated short-range interactions ($V^0_{\mathrm{sCA}}(R)$). These crystal properties are largely determined by the interplay between this potential and the Madelung energy because the remaining short-range interactions ($V^0_{\mathrm{sAA}}(x_{\mathrm{AA}}\,R)$ and $V^0_{\mathrm{sCC}}(x_{\mathrm{CC}}\,R)$) involve pairs of ions at considerably greater internuclear separations. Since these remaining interactions are considerably smaller than $V^0_{\mathrm{sCA}}\,(R)$, they were calculated from the modification (Lloyd & Pugh 1977) of electron gas theory (Gordon & Kim 1972) in which the exchange contribution to the interaction energy is corrected by a Rae-type factor (Rae 1974, 1975) calculated from the total number of valence electrons on both ions. Each ion was taken to contribute eight electrons to this number except for Li^+, Ag^+ and Pb^{2+} which were taken to contribute two, ten and twelve electrons respectively (Wood & Pyper 1981*c*).

The short-range potentials $V^0_{\mathrm{sCA}}(R)$ are reported in the Appendix.

(ii) *Computations with free ion wavefunctions*

Three main conclusions can be drawn from the results, presented in table 1, of calculations in which the wavefunctions of the free isolated ions are used to compute the short-range interactions (6.2) and (6.3).

First, the insufficient crystal cohesion for LiF, NaF and NaCl predicted (table 1) both with and without correlation and the undamped dispersion energy (6.4) shows that it is not sufficient to use free ion wavefunctions to calculate the short-range potentials. Hence the modifications of the ion wavefunctions caused by the crystalline environment must be considered if the crystal properties are to be described accurately. Although the dispersion energies calculated from (6.4) neglecting the corrections arising from the overlap of the ion wavefunctions will be too attractive (Kreek & Meath 1969; Jacobi & Csanak 1975), these energies are sufficiently small for LiF, NaF and NaCl that the overestimation of the dispersion does not mask the errors caused by the use of free ion wavefunctions.

The second conclusion to be drawn from the results with free ion wavefunctions is that the damping of the dispersion energy caused by the overlap of the ion wavefunctions cannot be

TABLE 1. PREDICTIONS OF CRYSTAL PROPERTIES FROM FREE ION WAVEFUNCTIONS(1)

		theory				
		no correlation		with correlation		
system		$V^0_{\mathrm{SCA}}(R)$ only(2)	all V^0_{S} (equation (6.1))	plus all V^0_{S}; no dispersion(3)	equation (6.3)	experiment
LiF	D_e	973	928	944	964	1036(4)
	R_e	4.05	4.31	4.24	4.15	3.80(5)
	B	5.80	3.49	4.43	5.53	6.98(6) 7.2(7) 8.67(8, 9)
NaF	D_e	880	863	880	908	923(4) 931(10)
	R_e	4.57	4.68	4.62	4.50	4.38(5)
	B	4.31	4.31	4.58	4.93	5.14(11) 5.17(10)
NaCl	D_e	718	701	720	749	773(12) 786(4)
	R_e	5.64	5.82	5.72	5.55	5.33(10)
	B	1.93	1.85	2.08	2.35	2.66(10) 2.74(14)
AgF	D_e	848	834	870	1040	942(13)
	R_e	4.85	4.95	4.85	4.36	4.66(15)
	B	4.60	4.43	5.19	9.13	—
PbF_2	D_e	2239	2201	2248	2395	2491(12)
	R_e	5.13	5.26	5.17	4.87	4.86(15)
	B	4.38	4.04	4.49	5.89	6.08(16) 6.27(17)

(1) The D_e lattice energy values are in kilojoules per mole; R_e in bohr; B in 10^{12} newtons per square metre extrapolated to low temperature, except PbF_2.

(2) Computed, including only nearest-neighbour cation–anion uncorrelated short-range interaction, i.e. $U^0_{\mathrm{L}}(R) = -M/R + n_{\mathrm{CA}}\, V^0_{\mathrm{SCA}}(R)$.

(3) Computed, including the short-range overlap-dependent correlation energy but excluding dispersion, i.e. from equation (6.3) with $U^{\mathrm{un}}_{\mathrm{disp}}(R)$ omitted.

(4) Weast (1979).
(5) Muhlhausen & Gordon (1981).
(6) Briscoe & Squire (1957).
(7) Kittel (1966).
(8) Susse & Rech (1961).
(9) Cohen & Gordon (1975).
(10) Vallin *et al.* (1966).
(11) Lewis *et al.* (1967).
(12) Johnson (1968).
(13) Tosi (1964).
(14) Firgate & Scheule (1966).
(15) Landolt-Börnstein (1973).
(16) Samara (1976).
(17) Rimai & Sladek (1980).

neglected. Thus the cohesion of AgF is seriously overestimated (table 1), as manifested by the too-large lattice energy and too-small R_e predicted when the dispersion energy is included in its undamped form (6.4). It is shown below that, for PbF_2, the agreement between experiment and the calculation with the undamped dispersion energy is fortuitous. This fortuitous agreement arises because the overestimation of the short-range repulsions (6.2) computed with the use of free ion wavefunctions cancels the overestimation of the attraction predicted by the undamped dispersion series.

The third conclusion shown by the computations with free ion wavefunctions is that the approximation previously used (Löwdin 1956; Froman & Löwdin 1962; Mansikka & Bystrand 1966; Vallin *et al.* 1967), which involved neglecting integrals involving charge densities constructed as products of different atomic orbitals belonging to the same ion, can yield misleading results. Comparison (table 2) with the present exactly computed results shows that

Table 2. Comparison of crystal properties predicted by using exact uncorrelated short-range interactions with predictions of Uppsala approximations⁽¹⁾

	LiF			NaF			NaCl		
	D_e	R_e	B	D_e	R_e	B	D_e	R_e	B
Löwdin (1956)	928	3.97	7.77	—	—	—	762	—	—
later Uppsala⁽²⁾	1003	3.89	5.9	952	4.20	5.0	763	5.1	2.54
RIP (Exact)	973	4.05	5.8	880	4.57	4.31	718	5.64	1.93

(1) All calculations used free ion wave functions and included only the uncorrelated short-range interaction between the closest cation–anion pairs, i.e. $U^0_L(R) = -M/R + 6V^0_{sCA}(R)$.

(2) LiF (Mansikka & Bystrand 1966), NaF (Vallin *et al.* 1967), NaCl (Petterson *et al.* 1967). Froman & Löwdin (1962) report $D_e = 765$ kJ mol^{-1} for NaCl.

use of these approximations overestimates the cohesion of LiF, NaF and NaCl calculated by including only the nearest cation–anion uncorrelated short-range interaction. These discrepancies are particularly severe for NaF. The failure of these approximations is also shown by the prediction (Hayns & Calais 1973) of 927 kJ mol^{-1} for the crystal binding energy of AgF at $R = 4.649$ a.u., compared with the result of 848 kJ mol^{-1} (column 1 of table 1) obtained when $V^0_{sCA}(R)$ is computed exactly from the free ion wavefunctions.

(iii) *Computations with ions calculated in a Watson potential*

The conclusion of the previous section, that the environmentally induced modifications of the ion wavefunctions cannot be neglected, motivates examination of the previously suggested method (Watson 1958; Pachalis & Weiss 1969; Schmidt *et al.* 1978) of simulating the environmental effects by means of the potential (Watson potential) arising from a shell of charge. In this method the ion wavefunctions are computed by adding to the free ion Dirac–Fock hamiltonian the electrostatic potential (the Watson potential) generated by a spherical shell of charge equal to the ionic charge but of opposite sign and having a radius equal to the ionic radius. Three main conclusions can be drawn from the results presented in table 3 of this series of calculations.

First, comparison of the first three columns of table 3 with those of table 1 shows that use of wavefunctions computed in the Watson potential predicts significantly greater crystal cohesion than the use of free ion wavefunctions. The variation principle can be used to test the quality of a wavefunction which describes a state containing only electrons and no positrons, when used to approximate the wavefunction of another system. It can therefore be concluded that use of the Watson potential is preferable to the neglect of environmentally induced wavefunction modifications.

The second conclusion, shown by the underestimation of the crystal cohesion (column 3) without the inclusion of dispersion, is that the dispersion contribution to the lattice energy should not be neglected. The discrepancies between the predictions of column 3 of table 3 and experiment correlate with the expected magnitudes of the dispersion contributions suggested by the C_6 and C_8 coefficients used, which are reported in table 4 of Pyper (1986). However, the results including dispersion (column 4 of table 3) for NaF, and particularly AgF, reinforce the conclusion drawn from the calculations with free ion wavefunctions that the damping of the dispersion arising from ion wavefunction overlap cannot be neglected.

The third conclusion that can be drawn from the results of table 3 is that use of the Watson

Table 3. Predictions of crystal properties from ion wavefunctions computed by using a Watson shell model⁽¹⁾

		theory				
		no correlation		with correlation		
		$V^0_{\mathrm{sCA}}(R)$ only⁽²⁾	all V^0_{s} (equation (6.1))	plus all V^0_{s}; no dispersion	equation (6.3)	experiment
LiF	D_e	1018	976	991	1017	1036
	R_e	3.90	4.09	4.05	3.98	3.80
	B	7.59	7.23	7.98	9.01	6.98, 7.2, 8.67
NaF	D_e	905	894	908	942	923
	R_e	4.45	4.54	4.48	4.36	4.38
	B	5.07	5.13	5.43	6.13	5.14, 5.17
NaCl	D_e	738	722	738	773	773, 786
	R_e	5.49	5.65	5.57	5.40	5.33
	B	2.38	2.32	2.54	2.94	2.66, 2.74
AgF	D_e	859	838	877	1066	942, 953
	R_e	4.74	4.87	4.77	4.30	4.66
	B	5.40	5.26	6.12	11.40	—
PbF_2	D_e	2258	2201	2276	2498	2491
	R_e	4.80	4.95	4.86	4.57	4.86
	B	7.37	6.83	7.89	10.45	6.08, 6.27

(1) For definitions, units and sources of experimental data see notes to table 1.

(2) Computed by using only the nearest-neighbour cation–anion uncorrelated short-range interaction, i.e. $U_{\mathrm{L}}(R) = -M/R + n_{\mathrm{CA}}\, V^0_{\mathrm{sCA}}(R) + E^{\mathrm{C}}_{\mathrm{Re}}(R) + mE^{\mathrm{A}}_{\mathrm{Re}}(R)$.

potential model does not always satisfactorily describe the environmentally induced modifications of the ion wavefunctions, and hence that this model should be regarded as unsatisfactory. Thus, for PbF_2 without dispersion, the Watson model exactly predicts the experimental R_e value while seriously underestimating the lattice energy and overestimating the compressibility (column 3). This combination of discrepancies with experiment is highly unphysical, indicating a basic failure of the calculation. Furthermore, because any inclusion of dispersion must reduce the predicted value of R_e, the agreement between the theory without dispersion and experiment must be regarded as fortuitous. The combination of excellent agreement between calculated and observed lattice energy, gross overestimation of the compressibility, and underestimation of R_e shown by the PbF_2 calculation with undamped dispersion, is also highly unphysical. The lower energy predicted by this calculation compared with the corresponding one (column 4 of table 1), which uses free ion wavefunctions, shows that the agreement between the experimental and calculated R_e value of the latter (table 1) calculation was fortuitous.

7. Conclusion

The basic formalism and numerical methods used in the RIP program to perform fully relativistic *ab initio* calculations for diatomic molecules have been described. The method of constructing the molecular wavefunction from Dirac–Fock atomic orbitals incorporates the properties of the isolated atoms to the greatest extent. This obviates the need for large basis sets to describe the core orbitals in the molecule, which are essentially unchanged from the atoms, thereby allowing the heaviest systems to be studied.

The program has been used to initiate a non-empirical study of ionic crystals containing the heaviest ions. This was not possible before the development of the RIP program because the interactions involving heavy ions showing large relativistic effects could not be computed. The results have both revealed the deficiencies of current methods for describing the influence of the crystalline environment on the ion wavefunctions and shown that it is unacceptable to neglect the damping of the interionic dispersion energy originating from non-negligible overlap of the ion wavefunctions (Kreek & Meath 1969). Methods for rectifying these two deficiencies to produce a physically sound and reliable method for studying ionic crystals are reported in the companion paper (Pyper 1986).

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APPENDIX

TABLE 4. UNCORRELATED SHORT-RANGE CATION–ANION INTERACTIONS COMPUTED WITH THE RIP PROGRAM(1)

	LiF		NaF		NaCl	
R	free	Watson	free	Watson	free	Watson
2.75	0.11539	0.10375	—	—	—	—
3.0	0.07028	0.06073	0.15657	0.14769	—	—
3.5	0.02724	0.02119	0.05716	0.05079	—	—
3.75	0.01728	0.01259	—	—	—	—
4.0	0.01107	0.00749	0.02209	0.01791	0.08104	0.07469
4.25	—	—	0.01398	0.01070	0.03586	0.03109
4.5	0.00467	0.00267	0.00895	0.00641	—	—
5.0	0.00203	0.00095	0.00381	0.00231	0.01622	0.01299
5.25	—	—	—	—	0.01098	0.00840
5.5	0.00090	0.00034	0.00166	0.00085	0.00750	0.00542
6.0	—	—	0.00074	0.00031	0.00354	0.00226
6.5	—	—	—	—	0.00170	0.00097
7.0	—	—	—	—	0.00083	0.00040
7.5	—	—	—	—	0.00040	0.00017

	AgF		PbF_2	
	free	Watson	free	Watson
3.5	0.10758	0.09907	—	—
4.0	0.03580	0.03016	0.09331	0.06586
4.5	0.01273	0.00927	0.04211	0.02493
4.75	0.00761	0.00500	0.02871	0.01523
5.0	0.00463	0.00268	0.01965	0.00915
5.5	0.00172	0.00069	0.00934	0.00305
6.0	0.00059	0.00009	0.00448	0.00076
6.5	—	—	0.00219	0.00003

(1) All measurements in atomic units; $V^0_{\mathrm{SCA}}(R)$ defined by equation (6.2).

TABLE 5. REARRANGEMENT ENERGIES FOR IONS COMPUTED IN POTENTIAL OWING TO A WATSON SHELL(1)

Li^+	Na^+	Ag^+	Pb^{2+}	F^-	Cl^-
0.00074	0.00091	0.00645	0.07116	0.00440	0.00321

(1) Here, $E_{\mathrm{Re}}(R)$ (equation (6.1)); for Watson shell, rearrangement energies are independent of R; all values in atomic units.