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Molecular States of Atoms. I. Orbital Energy Parameters

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Atomic valence state energies are analyzed to obtain values of orbital energy parameters that may be used in semiempirical molecular orbital calculations. Difficulty in defining the interaction between orbitals with non-integer electron populations is systematically avoided by distinguishing between a valence state and a "molecular state" of an atom, only the latter state having non-integer spin paired orbital occupancy. Application of the virial theorem to the molecular state enables a value for the orbital kinetic energy to be obtained from the valence state orbital energy parameters once an arbitrary configuration is defined as reference. The orbitals then are eigenfunctions of the atomic Fock operator for that reference molecular state and, with their energy parameters, may be employed as a fixed basis set for molecular orbital calculations.

Key words: Atomic orbital parameters – Valence state – kinetic energy – Virial theorem.

1. Introduction

Semi-empirical molecular orbital (MO) theories of the electronic structure of molecules and solids have received considerable attention for some time [1, 2]. The majority utilize the equations of Restricted Hartree–Fock (RHF) theory, with two-centre (molecular) integrals being either evaluated directly or related to the one-centre (atomic) integrals in the MO calculation. The atomic integrals may be considered as parameters, values for which can be related to the electronic

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structure of the constituent atoms in isolation. Techniques for obtaining requisite atomic parameters have been considered by *inter alia*, Oleari et al. [3], Cusachs et al. [4], and Sichel and Whitehead [5], using the concept of the atomic valence state (VS). Oleari et al. gave a general analysis of the method and presented parameters for the first two rows of the periodic table [3] and also for elements of the first and second transition series [6]. Sichel and Whitehead, working with the CNDO approximation, obtained parameters for the first four rows of (non-transition) elements. Cusachs et al. obtained parameters for the first and second row elements.

In this work we aim to obtain useful parameters for the first four rows of (non-transition) elements. Hinze analyzed [7] atomic spectroscopic state energies [8] to obtain "experimental" VS promotion energies which in turn may be analyzed by the method of Oleari et al. [3] to give a core-orbital interaction parameter U_a and inter-orbital interaction parameters $g_{aa'}$, a and a' denoting valence orbitals. The role of the self-interaction (intra-orbital exchange) energy has been the source of some difficulties of interpretation when attempting to calculate the energies of atomic states with non-integer orbital occupation. Oleari et al. proposed [3] that the form (correct for integer occupation number n_a) $\frac{1}{2}n_a(n_a-1)g_{aa}$ be the intra-orbital repulsion energy for all n_a in the range $0 \leq n_a \leq 2$. Sichel and Whitehead [5] and Cusachs et al. [4] implicitly used the more realistic (for MO theory) form $\frac{1}{4}n_a^2 g_{aa}$. We shall distinguish explicitly between an atomic VS, with integer orbital occupation numbers and possibly non-zero spin, and a zerospin single determinant *molecular state* (MS) with non-integer occupation numbers, when calculating self-interaction energies.

Sichel and Whitehead [5] calculated self-interaction contributions to atomic Fock matrix elements by assuming that all valence electrons were equally distributed amongst the available valence orbitals. Such Fock matrix elements turn out to be several electron volts smaller in magnitude than the corresponding "experimental" ionisation energies. Koopmans' theorem [9] predicts that the magnitudes of these two quantities are equal, while any correction to Koopmans' theorem due to "relaxation" of the final state should physically result in the ionisation energy being less than the Koopmans prediction. This deficiency in the Fock matrix elements is attributable to the above assumption; using an average orbital population to calculate the self-interaction terms in both initial and final states [5] fails to account for the considerable change in self-interaction energy contributed by the orbital from which ionisation occurs. We shall calculate our self-interaction terms without this assumption and show that the resulting Fock matrix elements are physically consistent with the ionisation energies used to determine the atomic parameters in the Fock matrix elements.

The core-orbital interaction parameter U_a accounts both for the kinetic energy of an electron in orbital a and the attractive interaction of that electron with the positive atomic core (nucleus plus core electrons). It is desirable to have separate "experimental" values for these two components of U_a and we give a prescription, based on the virial theorem, for obtaining them.

2. Molecular State of an Atom

An atomic valence state has a single Slater determinant many electron wave function, defined by assigning valence electrons to the available orbitals with a random spin distribution [3]. The VS energy E^{VS} is calculated by spin-averaging the exchange interactions between electrons in different orbitals; in contrast the exchange interaction between the electrons in a doubly occupied orbital is zero, consistent with the Pauli exclusion principle. Therefore [3]

$$E_A^{\mathrm{VS}} = C_A + \sum_a n_a U_a + \tfrac{1}{2} \sum_a \sum_{a' \neq a} n_a n_{a'} g_{aa'} + \tfrac{1}{2} \sum_a n_a (n_a - 1) g_{aa} \tag{1}$$

where the summations are over the valence orbitals of atom A, each occupied by $n_a(=0, 1 \text{ or } 2)$ electrons. C_A is the "core" contribution to the total atomic energy, independent of the valence electron configuration. The form of E_A^{VS} may either be interpreted using Hartree–Fock theory or simply considered as an expansion up to second order in the orbital occupation numbers [3]. The last term represents the Coulomb repulsion between the spin-paired electrons in each doubly occupied orbital. We shall not follow Oleari et al. [3] in retaining this term to predict the energy of configurations with non-integer occupation numbers. Instead we consider the single determinant RHF description of a closed shell (zero spin) molecule to obtain an expression for this energy.

The RHF energy of the molecule is [10]

$$E_{\mathrm{mol}} = \sum_A C_A + \sum_{uv} P_{uv} \left\{ H_{uv}^{\mathrm{mol}} + \tfrac{1}{2} \sum_{cd} P_{cd} [(uv|cd) - \tfrac{1}{2}(ud|cv)] \right\} \tag{2}$$

with u, v, c, d atomic orbital basis functions, $\boldsymbol{P}$ the density matrix, $\boldsymbol{H}^{\mathrm{mol}}$ the sum of the kinetic energy operator and the attractive potential of the positive atomic cores, and the two-electron interaction terms are given by the integrals

$$(uv|cd) = \iint \phi_u(1)\phi_v(1) r_{12}^{-1} \phi_c(2)\phi_d(2)\, d^3\boldsymbol{r}_1\, d^3\boldsymbol{r}_2 \tag{3}$$

with ϕ_v the wave function of atomic orbital u, etc. In the theoretical limit of atom A being removed to a very large distance from the other atoms of the molecule, without changing the spin paired non-integer occupation of the orbitals of A, the energy of A in this *molecular state* (MS) may be identified from (2) as

$$E_A^{\mathrm{MS}} = C_a + \sum_a n_a H_{aa}^A + \tfrac{1}{2} \sum_a \sum_{a' \neq a} n_a n_{a'} g_{aa'} + \tfrac{1}{4} \sum_a n_a^2 g_{aa}. \tag{4}$$

$\boldsymbol{H}^A$ is the sum of the kinetic energy operator and the core potential of A and we have used $P_{aa'} = n_a \delta_{aa'}$ to define the non-integer orbital occupation numbers n_a because we work with a minimal orthonormal basis. Also, as for the VS [3],

$$g_{aa} = (aa|aa) \tag{5}$$

$$g_{aa'} = (aa|a'a') - \tfrac{1}{2}(aa'|aa') \quad (\text{for } a' \neq a). \tag{6}$$

Because the electrons in all orbitals are spin paired the energy of a MS differs from a VS energy by the substitution of $\frac{1}{4}\sum_a n_a^2 g_{aa}$ for $\frac{1}{2}\sum_a n_a(n_a - 1) g_{aa}$. In other respects the interactions in the valence state and molecular states are the same; if the parameters in (1) are determined by fitting that equation to several known valence state energies then we have obtained the interaction terms $H^A_{aa} = U_a$ and the $\{g_{aa'}\}$ required for a semiempirical molecular orbital (MO) calculation. Associated with E^{MS}_A is the Fock operator $\boldsymbol{F}^A$, with diagonal matrix elements

$$F^A_{aa} = H^A_{aa} + \sum_{a' \neq a} n_{a'} g_{aa'} + \tfrac{1}{2} n_a g_{aa} \tag{7}$$

which reproduces the valence electron contribution to the total energy i.e.

$$E^{\text{MS}}_A = C_A + \tfrac{1}{2} \sum_a n_a (F^A_{aa} + H^A_{aa}). \tag{8}$$

Koopmans' theorem [8] ($-F_{aa}$ = the ionisation energy, provided there is no relaxation of the final state electron distribution) should apply to ionisation of an electron from an orbital with $n_a = 2$. The final state f will have an unpaired electron in a and unchanged occupancy of the other orbitals. The total change in self-interaction energy is then $-g_{aa}$ and

$$\begin{aligned} I_a &= E^f_A - E^{\text{MS}}_A (n_a = 2) \\ &= -H^A_{aa} - \sum_{a' \neq a} n_{a'} g_{aa'} - g_{aa} = -F^A_{aa} (n_a = 2) \end{aligned}$$

consistent with Koopmans' theorem.

3. Approximations and Constraints

Now we consider what approximations are desirable in the analysis of the "experimental" valence state energies. The energies and wave functions obtained from a molecular orbital calculation should be invariant with respect to unitary transformations of the space fixed axes defining nuclear positions and basis orbital orientations. This is equivalent to requiring invariance with respect to unitary transformations that mix the basis orbitals within any given atomic subshell. Approximating the calculation of two-electron integrals can destroy such invariance [11]; for the p valence subshell, which is relevant for the atoms considered in this work, invariance is retained provided

$$(xy|xy) = \tfrac{1}{2}[(xx|xx) - (xx|yy)]$$

and similarly for the other relatively small but non-zero one centre two-electron integrals $(xz|xz)$ and $(yz|yz)$. In many semiempirical MO calculations such integrals are set to zero, through application of either the Mulliken [12] or Zero Differential Overlap (ZDO) [13] approximations. We therefore accept this restriction and preserve this invariance by setting $g_{xx} = g_{xy} = g_{pp}$ throughout, thereby reducing the number of parameters in E^{VS}_A from 7 to 6.

The number of valence state energies available (see Table 2) varies from 7, for elements near the end of a row of the periodic table, up to 16 for group IV elements. An initial analysis of the VS data with the 6-parameter formula indicated that, for most elements, an empirical relationship

$$g_{sp} \simeq \tfrac{2}{5} g_{ss} + \tfrac{3}{5} g_{pp} \tag{9}$$

was satisfied to within a fraction of 1 eV. Exceptions were some of the alkali and halogen elements for which g_{sp} was, unrealistically, not similar in magnitude to g_{ss} and g_{pp}. This was taken to be a reflection of the known relatively poor quality of VS data for these elements [3, 7]. Therefore the number of independent parameters was further reduced to 5 by adopting Eq. (9), so that (with $n_p = n_x + n_y + n_z$)

$$E_A^{\mathrm{VS}} = C_A + n_s U_s + n_p U_p + \{\tfrac{1}{4} n_s^2 + \tfrac{2}{5} n_s n_p\} g_{ss} + \{\tfrac{3}{5} n_s n_p + \tfrac{1}{2} n_p (n_p - 1)\} g_{pp}. \tag{10}$$

The adoption of Eq. (9) had a negligible effect on the values obtained of the remaining 5 independent parameters for those elements for which Eq. (9) held previously, while g_{ss} and g_{pp}, for the few alkali and halogen elements that had been unsatisfactory, now had values compatible with those of their neighbours in the periodic table.

4. Orbital Kinetic Energy

$H_{aa} = U_a$ is not of immediate use in all semiempirical MO theories. We write

$$H_{aa} = T_{aa} - Z_A \Lambda_a \tag{11}$$

with T_{aa} a matrix element of the kinetic energy operator, Z_A the net positive charge of the core of A and $-Z_A \Lambda_a$ the potential energy of a valence electron due to interaction with this core. Off-diagonal matrix elements of $\boldsymbol{H}$ are evaluated using empirical β^0 bonding parameters [1] in most ZDO theories and then T_{aa} and Λ_a are not required, H_{aa} being sufficient. If any attempt is to be made to calculate two-centre kinetic energy matrix elements explicitly e.g. using the Rüdenberg approximation [14], then some means is needed of obtaining a value of T_{aa} from the experimental parameter U_a.

The virial theorem states that for a many-electron system in equilibrium the total kinetic energy KE is related to the total potential energy PE by KE $= -\frac{1}{2}$PE. Thus for an equilibrium molecular state of atom A

$$2 \sum_a n_a T_{aa} - Z_A \sum_a n_a \Lambda_a + \tfrac{1}{2} \sum_a n_a \left[\sum_{a' \neq a} n_{a'} g_{aa'} + \tfrac{1}{2} n_a g_{aa} \right] = 0. \tag{12}$$

Our prescription for obtaining T_{aa} is to set *each term* in the summation over a in Eq. (12) to zero. Physically this corresponds to assuming that each valence electron interacts with the core and other valence electrons through pure Coulombic interaction, which is not strictly exact because of penetration of the core electron cloud by the valence electrons. This prescription supplies an orbital virial relation (OVR) for each valence orbital

$$2 T_{aa} - Z_A \Lambda_a + \tfrac{1}{2} \sum_{a'} n_{a'} g_{aa'} - \tfrac{1}{4} n_a g_{aa} = 0 \tag{13}$$

which, together with Eq. (11), provides values of T_{aa} and Λ_a which ensure that $\mathrm{KE} = -\frac{1}{2}\mathrm{PE}$ for atom A. Naturally for hydrogen and helium, with only a 1*s* occupied valence orbital, Eq. (13) is an exact statement of the virial theorem.

To use the OVR a choice of a reference molecular state is required so that the occupation numbers for use in (13) are defined. Applying the virial theorem to this reference MS implies that the set of valence orbitals $\{a\}$ must then be the eigenfunctions of the Fock operator $\boldsymbol{F}^A$ for this state, because the virial theorem holds for states for which the expectation value of the many-electron Hamiltonian is a minimum. We choose the reference MS, for all elements, to be the neutral atom with equal occupation of all the valence atomic orbitals. For an sp^3 valence shell (with a bar denoting an occupation number for the reference state)

$$\bar{n}_s = \bar{n}_x = \bar{n}_y = \bar{n}_z = \tfrac{1}{4}Z_A \tag{14}$$

and for hydrogen and helium $\bar{n}_s = Z_A$. Writing

$$G_a = \tfrac{1}{2}\sum_{a'} \bar{n}_{a'}(1 - \tfrac{1}{2}\delta_{aa'})g_{aa'} \tag{15}$$

we obtain $T_{aa} = -U_a - G_a$ (16)

$$Z_A\Lambda_a = -2U_a - G_a. \tag{17}$$

Rewriting Eq. (15) for the reference MS we obtain, for hydrogen and helium

$$G_s = \tfrac{1}{4}Z_A g_{ss}$$

and for the elements with sp^3 valence shells

$$G_s = \tfrac{1}{16}Z_A(g_{ss} + 6g_{sp})$$

$$G_p = \tfrac{1}{16}Z_A(2g_{sp} + 5g_{pp}).$$

In this way, for each element, values of T_{aa}, Λ_a and g_{aa} are obtained from atomic spectral data, via a valence state analysis, for valence orbitals that are eigenfunctions of a well defined reference molecular state of an atom of that element.

5. Results

The valence state energies were calculated from Hinze's data on promotion energies (to valence states from the ground spectroscopic state X) for a large number of atoms and ions [7]. Energy differences between valence states of different ions of the same element have been determined by using the appropriate [7] ionisation energies and electron affinities. For illustration we give in Table 1 available VS energies of a neutral carbon atom and its singly charged ions, relative to the ground spectroscopic state of atomic carbon. All energies and orbital parameters here are in units of eV. For each element the five orbital parameters in Eq. (10) were then calculated using multiple linear regression analysis and are presented in Table 2.

Valence states of the neutral atom and singly charged ions were considered in most cases. The exceptions were the inert gas elements, calcium and strontium

Table 1. Valence state energies in eV for C^0, C^+ and C^- calculated from the promotion energies in Ref. [7]. The energy zero is defined by the ground spectroscopic state of the neutral carbon atom

n_s	n_x	n_y	n_z	E^{VS}
2	1	0	0	11.260
1	2	0	0	21.521
0	1	2	0	31.260
1	1	1	0	19.752
0	1	1	1	29.471
2	2	0	0	1.677
0	2	2	0	19.186
2	1	1	0	0.325
1	2	1	0	9.832
0	1	2	1	17.834
1	1	1	1	8.479
2	2	1	0	0.768
1	2	2	0	9.340
0	2	2	1	17.628
2	1	1	1	−0.438
1	2	1	1	8.134

for which, in the absence of data for the negative ion, states of the A^{++} ion were considered. Only negative ion valence states with two s electrons were used (except for the alkali elements) because the promotion energies to other negative ion valence states, e.g. 1220, 0221 and 1211 in Table 1, had been obtained by extrapolation rather than directly from experiment [7]. For the alkali elements all available negative ion valence states were required to determine g_{ss} and g_{pp}, the values for which are therefore less reliable than for other elements. For I^+ the promotion energy ($X \rightarrow p^6$) was taken to be 33.165 eV rather than 23.165 eV [7] to give a value similar to that for the other halogen elements and consistent with the other I^+ promotion energies of 12.984 eV ($X \rightarrow s^2x^2y^2$), 11.143 eV ($X \rightarrow s^2x^2yz$) and 21.147 eV ($X \rightarrow sx^2yz$). Otherwise Hinze's data were used without modification.

The results are given to 3 decimal places to facilitate checks on the orbital parameters in Table 2, which should reproduce the VS energies used, within the limitation of the approximation $g_{xx} = g_{xy} = g_{pp}$. Such checks suggest that the parameter values are physically significant as far as the first decimal place. However it would probably be sensible to carry through any MO calculation with the values to 3 decimal places to avoid introducing errors due to premature rounding-off.

6. Discussion

In this work we have explicitly distinguished between the valence state of an atom, defined by integer occupation of atomic orbitals, and the molecular state

Table 2. Orbital energy parameters in eV for all the non-transition elements with atomic number ≤ 54. g_{ss} and g_{pp} are obtained from fitting Eq. (10) to the available valence state energies for each element, the other parameters being calculated from U_s and U_p (see Sect. 4). NVS denotes the number of valence state energies used in determining the 5 independent parameters in Eq. (10)

	T_{ss}	Λ_s	g_{ss}	T_{pp}	Λ_p	g_{pp}	NVS
H	10.388	23.988	12.850	—	—	—	3
He	39.490	46.945	29.820	—	—	—	3
Li	3.694	9.065	4.570	2.117	5.679	3.139	7
Be	10.399	13.014	6.254	6.508	9.035	5.714	7
B	20.931	17.734	9.184	14.215	13.085	8.127	11
C	33.757	21.536	11.761	23.622	16.116	9.593	13
N	48.536	24.727	12.095	35.346	19.467	12.190	13
O	68.737	29.386	17.925	46.062	20.839	11.841	10
F	83.151	30.290	13.875	65.317	25.529	15.931	7
Ne	115.409	37.220	16.017	96.378	33.444	22.062	7
Na	3.531	8.654	4.670	1.784	4.837	2.672	7
Mg	9.312	11.470	5.968	5.498	7.329	3.954	7
Al	16.778	14.061	7.289	10.789	9.843	5.898	11
Si	27.014	17.200	10.905	18.039	11.935	6.116	13
P	38.894	20.340	13.864	27.921	15.023	8.160	13
S	42.805	18.372	10.212	32.869	14.798	8.596	10
Cl	54.704	20.092	9.571	45.574	17.681	10.792	7
Ar	74.798	24.392	12.482	62.614	21.513	13.511	7
K	2.550	6.520	2.885	1.563	4.659	3.584	7
Ca	6.309	9.122	5.760	4.058	7.083	7.063	7
Ga	15.614	13.044	4.959	9.945	9.600	7.024	11
Ge	30.091	19.323	14.190	19.408	12.586	5.608	13
As	34.532	18.041	10.581	27.163	14.804	8.800	13
Se	45.742	19.934	13.579	33.034	14.791	8.003	10
Br	55.829	20.807	12.718	42.609	16.519	9.571	7
Kr	68.170	22.112	11.080	55.969	19.223	12.069	7
Rb	2.835	6.948	4.180	1.786	4.454	1.735	7
Sr	6.082	8.577	5.340	3.941	6.551	6.046	7
In	16.876	14.000	6.969	10.290	9.394	5.641	11
Sn	24.510	15.368	9.593	15.616	10.137	4.774	13
Sb	36.759	19.275	13.820	25.560	13.731	7.266	13
Te	45.132	19.765	14.760	31.018	13.805	7.040	10
I	46.925	17.156	9.622	34.449	13.258	7.572	7
Xe	57.704	18.701	8.951	48.719	16.713	10.545	7

which has spin-paired, generally non-integer, orbital occupation. This enables us to take over the orbital energy parameters obtained from valence state energies into a MO calculation without encountering conceptual difficulties in accounting for the self-interaction energy. Gopinathan and Whitehead [15] have also discussed the calculation of the intra-orbital repulsion energy and have proposed it be calculated as $[\frac{1}{2}n'_a(n'_a-1)+n'_a f_a]g_{aa}$, where $n_a = n'_a + f_a$ and n'_a is the largest integer $\leq n_a$. This differs in detail from $\frac{1}{4}n_a{}^2 g_{aa}$ but also removes the physically unacceptable attraction between electrons in the same orbital predicted by $\frac{1}{2}n_a(n_a-1)g_{aa}$ for $0<n_a<1$.

Once a fixed basis set is defined as reference, matrix elements of the Fock operator $\boldsymbol{F}^A$ (Eq. (7)) are also defined. The reference configuration has been chosen realistically as a typical configuration of the atom when in a molecule, with electrons shared equally amongst the available valence orbitals. Defining the Fock operator for unoccupied (virtual) valence orbitals poses no problem however. If e.g. a $2s^12p^0$ reference configuration for lithium were preferred then the appropriate values of G_s and G_p could be calculated using Eq. (15). T_{ss}, Λ_s, T_{pp}, Λ_p, would then follow from Eqs. (16) and (17), using Eq. (11) to obtain U_a from Table 2.

Valence orbital interaction parameters have been obtained for hydrogen, helium and all the non-transition elements of the first four rows of the periodic table. These include values for the inert gases, not to our knowledge previously obtained from spectroscopic data. Naturally MO calculations with just a basis of occupied orbitals for these atoms are not usually contemplated, but at least the parameters can aid our understanding of the isolated inert gas atoms, and help in the study of trends in the parameter values with position in the periodic table.

In the main these trends conform to established concepts of atomic structure. The parameters tend to increase with increasing electronegativity across the periodic table and decrease for the heavier elements in any given group (column). g_{ss} and g_{pp} are found to exhibit significant differences within these overall trends. Values of g_{ss} here appear to peak near the middle of any given row, while g_{pp} increases steadily across each row. It appears that as a valence shell fills the total repulsion energy between valence electrons, for given g_{aa} roughly proportional to Z_A^2, increasingly offsets the attraction due to the nucleus and core electrons, $\propto Z_A$, thereby inhibiting a steady increase of g_{ss} and g_{pp}. This has two important consequences in the analysis of valence state energies: (1) attempts to "smooth" a set of g_{aa} values e.g. to make $g_{aa}\propto Z_A$, in order to make a set of somewhat scattered values more acceptable intuitively, may be ill-founded; (2) the marked differences between g_{ss} and g_{pp} for most elements indicate that the assumption $g_{ss}=g_{pp}=g_{AA}$ can be poor.

Values of T_{aa} and Λ_a have been obtained from the parameter $U_a=T_{aa}-Z_A\Lambda_a$ by using the OVR discussed in Sect. 4. For hydrogen all the MS parameters are less than for the free atom, indicating that the electron density for a hydrogen atom in a molecule is described by a more diffuse orbital than the $1s$ exponential atomic orbital. This is a consequence of the repulsion between two $\frac{1}{2}$-electrons in the hydrogen atom MS. The orbital kinetic energies T_{aa} increase steadily with Z_A to offset the increasing attraction due to the core, $-Z_A\Lambda_a$. Because the g_{aa} do not exhibit the same trends the implication is that the radial factors of the wave functions of the valence orbitals will change their detailed shape with Z_A. Such wave functions are being calculated using these orbital parameters and will be reported shortly [16].

The use of the OVR to obtain T_{aa} and Λ_a enabled a reference MS to be defined unambiguously for each element. MO calculations using these parameters should therefore employ the valence orbitals of this reference MS in a fixed basis set. It is interesting to observe that a form of Extended Hückel Theory (EHT) can be derived from the RHF equations if $T_{aa} = -F_{aa}^A$ (the virial theorem for a one-electron atom) is assumed [17, 18]. That equation clearly violates the virial theorem for a many-electron atom; however it only affects EHT in the calculation of two-centre kinetic energy matrix elements which in practice is subsumed into the value or functional form employed for the Wolfsberg–Helmholz parameter K.

Finally we should note that Λ_a in this work is not the same core-orbital interaction parameter as is used in the analysis of core level chemical shifts [19] observed in X-ray photoelectron spectroscopy (XPS). That analysis requires λ_a, the interaction between the core orbital studied and the valence orbital a. Λ_a is representative of the overall interaction of a with the nucleus and all core electrons. For the valence p subshell penetration of the core should be small and then $\lambda_p \simeq \Lambda_p \simeq \langle r^{-1}\rangle_p$. Values of Λ_p here are in reasonable agreement with theoretical estimates of $\langle r^{-1}\rangle_p$ obtained by Politzer and Daiker [20] for some of the elements we have considered. As it is possible that the p subshell population is more sensitive to chemical environment than the s subshell, these values of Λ_p may well aid the analysis of XPS chemical shifts.

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References

1. Sigma molecular orbital theory, O. Sinanoğlu and K. B. Wiberg, Eds. Yale: Yale Univ. Press 1970
2. del Re, G., Berthier, G., Serre, J.: Electronic states of molecules and atomic clusters Berlin: Springer Verlag 1980
3. Oleari, L., di Sipio, L., de Michelis, G.: Mol. Phys. **10**, 97 (1966)
4. Cusachs, L. C., Reynolds, J. W.: J. Chem. Phys. **43**, S160 (1965); Cusachs, L. C., Reynolds, J. W., Barnard, D.: J. Chem. Phys. **44**, 835 (1966)
5. Sichel, J. M., Whitehead, M. A.: Theoret. chim. Acta (Berl.) **7**, 32 (1967)
6. di Sipio, L., Tondello, E., de Michelis, G., Oleari, L.: Chem. Phys. Letters **11**, 287 (1971)
7. Hinze, J.: Ph.D. thesis. Univ. of Cincinnati 1962
8. Moore, C. E.: Nat. Bur. Stand. Circ. 467. Washington 1949, 1952 and 1958
9. Koopmans, T.: Physica **1**, 104 (1933)
10. Roothaan, C. C. J.: Rev. Mod. Phys. **23**, 69 (1951)
11. Pople, J. A., Santry, D. P., Segal, G. A.: J. Chem. Phys. **43**, S129 (1965)
12. Mulliken, R. S.: J. Chem. Phys. **46**, 497, 675 (1949)
13. Parr, R. G.: J. Chem. Phys. **20**, 239 (1952)
14. Ruedenberg, K.: J. Chem. Phys. **19**, 1433 (1951)
15. Gopinathan, M. S., Whitehead, M. A.: Israel J. of Chem. **19**, 209 (1980)
16. Parry, D. E.: in preparation
17. Cusachs, L. C., Cusachs, B. B.: J. Phys. Chem. **71**, 1060 (1967)

18. Parry, D. E.: J.C.S. Faraday II **73**, 774 (1977)
19. Parry, D. E.: J.C.S. Faraday II **71**, 337 (1975)
20. Politzer, P., Daiker, K. C.: Chem. Phys. Letters **20**, 309 (1974)

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