Theor Chim Acta (1996) 94: 187–203

Theoretica Chimica Acta

Core and valence electrons in atoms and ions: configuration interaction calculations*

Normand Desmarais, Sándor Fliszár

Département de Chimie, Université de Montréal, C.P. 6128, Succ. Centre-ville, Montréal, Québec, H3C 3J7 Canada

Received February 20, 1996 / Final version received April 25, 1996 / Accepted April 26, 1996

Summary. The partitioning of ground-state atoms or ions into inner spherical cores with radius r_b and outer valence regions extending from r_b to infinity is explored with the help of the expression $E^v = \frac{1}{3}(T^v + 2V^v)$ for the valence-region energy (where T^v and V^v are, respectively, the kinetic and potential energies of the 'valence electrons' N^v found beyond the boundary surface defined by r_b) using also the appropriate expression for E^{ion}, the energy of the ion left behind after removal of the valence electrons. E^v and E^{ion} are meaningful only for discrete numbers, N^c, of electrons assigned to the core, namely, when the exchange integrals, K^{cv}, between N^c and N^v total (or at least closely approach) 0, i.e., for $N^c = 2$ e or $N^c = 2$ and 10 e for the first- or second-row elements, respectively.

Keywords. Atoms – Core-valence partitioning – Configuration interaction

1 Introduction

The partitioning of ground-state atoms or ions into core and valence regions reflects the old idea that chemical properties are largely governed by the outer (or *valence*) atomic regions, i.e., by what we shall call valence electrons. Though intuitively appealing, this partitioning is not cast in formal theory. The question as to whether a core–valence separation can be defined in a physically meaningful way is thus sensible. Surely, introduction of a suitable criterion is required to provide an acceptable operational definition.

A familiar way of handling this question is offered by the notion of *electronic shells*. By definition, an electronic shell collects all the electrons with the same principal quantum number. The K shell, for example, is made of 1*s* electrons, the L shell collects the 2*s* and 2*p* electrons, etc. The valence shell thus consists of the last occupied electronic shell, while the *core* consists of all the inner shells. This segregation into electronic shells is justified by the well-known order of the successive ionization potentials of the atoms.

Now, in what we call the *Hartree–Fock orbital space* – or simply *orbital space* – the total energy is partitioned from the outset into orbital energies, $\varepsilon_i = \varepsilon_{1s}$, ε_{2s}, etc.

---

* Part of the projected Ph.D. dissertation of N. D.

So we can always consider a collection of electrons and deduce their total energy from the appropriate sum of their orbital energies, remembering, however, that one must also correct for the interelectronic repulsions which are doubly counted in any sum of Hartree–Fock eigenvalues. No special problem arises with core-valence separations in the orbital space but it is still up to us to select the core (or valence) electrons as seems appropriate. It appears reasonable to use the order of orbital energies as a guideline and thus to consider the $1s^2$ electrons as the core of the first-row elements or the $1s^2$, $2s^2$ and $2p^6$ electrons for the second row. Briefly, we re-encounter the familiar shell model. Finally, let us mention that the essence of the so-called 'pseudopotential' methods [1] is to replace core electrons by an appropriate operator. The point is that the core-valence partitioning involved in these methods refers to the same orbital space as the corresponding all-electron calculations.

What now if we abandon the orbital-by-orbital electron partitioning in favor of a description based on the stationary ground-state electron density $\rho(\mathbf{r})$? Clearly, this will oblige us to redefine the core-valence separation. In sharp contrast with what was done in orbital space, we will need a *partitioning in real space.* We consider an inner *spherical* core, centered at the nucleus, with radius r_b, and an outer valence region extending from r_b to infinity. The number of core electrons, N^c, is then

$$N^\mathrm{c} = 4\pi \int_0^{r_\mathrm{b}} r^2 \rho(r)\,\mathrm{d}r \tag{1}$$

where $\rho(r)$ is the electron density[1] at a distance r from the nucleus with charge Z. The definition of N^c now rests with the definition of the proper r_b. A number of suggestions were offered to that effect [3]–[13]. Let us briefly examine them.

Politzer et al. [3]–[5] define the 'average ionization potential at the point $\mathbf{r}$'

$$\bar{I} = \sum_i \frac{\rho_i(\mathbf{r})|\varepsilon_i|}{\rho(\mathbf{r})}$$

where $\rho_i(\mathbf{r})$ is the electron density of the orbital with energy ε_i and $\rho(\mathbf{r}) = \sum_i \rho_i(\mathbf{r})$ is the total electron density at the point $\mathbf{r}$. $\bar{I}$ can be interpreted as the average energy required for the removal of one electron from the point $\mathbf{r}$ of an atom or a molecule. In ground-state atoms, $\bar{I}$ decreases in a piecewise manner along the coordinate r [5] and the regions between the inflexion points may be taken as electron shells. Indeed, the numbers of electrons contained in the sphere with radius r_b, Eq. (1), are close to 2 for the first-row elements (e.g., 2.033 e for carbon and 2.030 e for neon) or close to 2 and 10 e for the larger atoms (e.g., 2.011 and 10.068 e for argon)[2].

The 'average local electrostatic potential', $V(r)/\rho(r)$, introduced by Politzer [6] led Sen and coworkers [7] to propose the conjecture that the global maximum in $V(r)/\rho(r)$ defines the location of the core–valence separation in ground-state atoms. Using this criterion, one finds N^c values, Eq. (1), of 2.065 and 2.112 e for carbon and neon, respectively, and 10.073 e for argon, which are reasonable estimates in light of what we know about the electronic shell structure. Politzer [6] also made the significant observation that $V(r)/\rho(r)$ has a maximum any time the radial distribution function, $D(r) = 4\pi r^2 \rho(r)$, is found to have a minimum.

---

[1] We write $\rho(\mathbf{r}) = \rho(r)$ because of the spherical symmetry of the electronic density; see [2].

[2] This result is well substantiated for the atoms Li–Ca but less clear for atoms with d electrons, probably because of the interpenetration of sub-shells in the heavier atoms [4].

This minimum of $D(r)$ plays a major role in the Politzer–Parr approximation [9][3] for the valence-region energy of ground-state atoms

$$E^{\mathrm{v}} = -\frac{3}{7}(Z - N^{\mathrm{c}}) \int_{r_{\mathrm{b}}}^{\infty} 4\pi r \rho(r)\,\mathrm{d}r \tag{2}$$

where the boundary surface separating the inner core and the outer valence regions is taken at $r_{\mathrm{b}} = r_{\mathrm{min}}$, i.e., at the minimum of the radial distribution function. In Hartree–Fock calculations, minima of $D(r)$ occur approximately at the 'right places' (from the viewpoint of the shell model), i.e., at $N^{\mathrm{c}} \simeq 2$ e for the first-row and at $N^{\mathrm{c}} \simeq 2$ and $N^{\mathrm{c}} \simeq 10$ e for the second-row elements. This result sheds light on the physical involvement of the electronic shell structure in a meaningful separation of an atom or ion into core and valence regions but should evidently not be taken too literally with Hartree–Fock wave functions.

An alternate criterion is rooted in the properties of exchange integrals. Two-electron integrals carried out within appropriate spatial integration limits describe $|1/r_{12}|$ interactions between electrons assigned to the core region τ^{c} and electrons associated with the valence space τ^{v}. This concerns both Coulomb and exchange integrals. Consider the sum, K^{cv}, which collects all the relevant exchange terms between the core electrons found in τ^{c} and the valence electrons found in τ^{v}. This sum can vanish, i.e., $K^{\mathrm{cv}} = 0$ is possible. (The function $1s(1)2s(1)1s(2)2s(2)$, for example, can be positive or negative depending on whether r_1 and r_2 are on the same side or on opposite sides of the nodal surface. The final sign of this contribution thus depends on the locations of the boundary and nodal surfaces.) Nonzero exchange integrals between individual electrons are a consequence of their indistinguishability. It seems natural to argue that a group of electrons should not be distinguished from another group of electrons if the total exchange between these groups is nonzero and that a vanishing K^{cv} should thus accompany a discrimination between core and valence electrons. Self-consistent field (SCF) calculations fully support this view. For the first-row elements, the K^{cv} integrals vanish near the points corresponding to $N^{\mathrm{c}} \simeq 2$ e. For the second-row elements, these integrals vanish near the points corresponding to $N^{\mathrm{c}} = 2$ and $N^{\mathrm{c}} = 10$ e. From nickel onwards, however, no boundary can be detected for $N^{\mathrm{c}}=28$ e – an observation which is consistent with a relatively significant degree of interpenetration, for third-row atoms, between the $3d$, $4s$, or $4p$ electrons and the $3s$ or $3p$ electrons, as shown by Politzer and Daiker [16].

While it seems relatively straightforward to define core and valence electrons in the *orbital space*, things are visibly somewhat more involved in *real space*. Still it is certainly reassuring to find recognizable features suggesting a meaningful definition of boundary surfaces. We shall test them numerically, but SCF results are not quite sufficient to do the job to our satisfaction. Here we use configuration interaction (CI) wave functions and an energy formula for E^{v} deduced earlier [11]–[13] to get to the heart of the matter.

---

[3] In Thomas–Fermi theory, the ground-state energy of a neutral atom with nuclear charge Z is [14, 15] $E = \frac{3}{7} Z^2 \phi_0'$, where

$$\phi_0' = \left(\frac{\delta\phi(r)}{\delta r}\right)_{r=0} = \left(\frac{\delta(rV/Z)}{\delta r}\right)_{r=0},$$

$V(r)$ being the total electrostatic potential at the distance r from the nucleus. Politzer and Parr applied this Thomas–Fermi formula to a hypothetical neutral atom containing $(Z - N^{\mathrm{c}})$ electrons in the field of an expanded effective nucleus of radius $r_{\mathrm{b}} = r_{\mathrm{min}}$ to get Eq. (2).

2 Core and valence electrons in real space: working formulas

Let us briefly review the quantities involved in our core–valence partitioning. With reference to the partitioning surface defined by r_b, the numbers of core electrons, N^c, and of valence electrons, N^v, are readily obtained by adequately integrating the electron density $\rho(\mathbf{r})$ between 0 and r_b or between r_b and ∞, respectively, using $dN = \rho\, d\tau = 4\pi r^2 \rho(r)\, dr$. The nuclear–electronic potential energy, $-Z\int[\rho(\mathbf{r})/r]\,d\tau$, is V_{ne}^c for the N^c core electrons and V_{ne}^v for the N^v valence electrons with kinetic energies T^c and T^v, respectively, obtained by appropriate selections of the integration limits.

Now we come to the two-electron integrals. The interelectronic repulsion, V_{ee}, is split into three parts, namely: *i)* V_{ee}^{cc} = electron–electron repulsion concerning only the charges of the core region, *ii)* V_{ee}^{vv}, the repulsion between valence electrons, and *iii)* V_{ee}^{cv}, the repulsion between the N^c core and the N^v valence electrons, with $V_{ee} = V_{ee}^{cc} + V_{ee}^{vv} + V_{ee}^{cv}$. Evaluation of these quantities involves integrations over the spatial coordinates of two electrons, say, electrons 1 and 2, with $d\tau_1 = r_1^2 \sin\theta_1\, d\theta_1\, d\varphi_1\, dr_1$ and a similar expression for $d\tau_2$. Let us write these integrals in shorthand notation, e.g.,

$$I = \int^{\tau_1}\int^{\tau_2} \ldots d\tau_1\, d\tau_2$$

for the full integration range, τ_1 and τ_2, of electrons 1 and 2, respectively. These two-electron integrals are conveniently separated into three contributions [11]–[13], namely

$$I^{cc} = \int^{\tau_1^c}\int^{\tau_2^c} \ldots d\tau_1\, d\tau_2 \tag{3}$$

$$I^{vv} = \int^{\tau_1^v}\int^{\tau_2^v} \ldots d\tau_1\, d\tau_2 \tag{4}$$

$$I^{cv} = \int^{\tau_1^v}\int^{\tau_2^c} \ldots d\tau_1\, d\tau_2 + \int^{\tau_1^c}\int^{\tau_2^v} \ldots d\tau_1\, d\tau_2 \tag{5}$$

(with $I = I^{cc} + I^{vv} + I^{cv}$) for the calculation of the V_{ee}^{cc}, V_{ee}^{vv} and V_{ee}^{cv} repulsion energies, respectively. This completes the breakdown of the kinetic and potential energies into core and valence contributions, for future use.

In this work, the relevant energies are E^v, the energy of the valence electrons, and E^{ion}, that of the ion left behind upon removal of the N^v valence electrons, with $E^v + E^{ion} = E^{atom}$, the ground-state energy of the parent atom. Clearly, E^v is *not* simply the sum of the kinetic and potential energies of the electrons in the outer (valence) region, as one would calculate them from their stationary densities. The valence energy described here accounts for any relaxation that accompanies an actual removal of the appropriate number of valence electrons. From Hartree–Fock theory we get [11, 13]

$$E^v = \frac{1}{3}\left(V_{ne}^v + V_{ee}^{cv} + \sum_i N_i^v \varepsilon_i\right) \tag{6}$$

where ε_i is the eigenvalue of orbital i and N_i^v the number of valence electrons of this orbital. On the other hand [12, 13]

$$\sum_i N_i^{\mathrm{v}} \varepsilon_i = T^{\mathrm{v}} + V_{\mathrm{ne}}^{\mathrm{v}} + 2V_{\mathrm{ee}}^{\mathrm{vv}} + V_{\mathrm{ee}}^{\mathrm{cv}} \tag{7}$$

so that (6) becomes

$$E^{\mathrm{v}} = \frac{1}{3}\left(T^{\mathrm{v}} + 2V^{\mathrm{v}}\right) \tag{8}$$

where $V^{\mathrm{v}} = V_{\mathrm{ne}}^{\mathrm{v}} + V_{\mathrm{ee}}^{\mathrm{vv}} + V_{\mathrm{ee}}^{\mathrm{cv}}$ is the total potential energy of the valence electrons. Orbital eigenvalues are thus not directly involved in the energy formula giving E^{v}. Finally, with $E^{\mathrm{ion}} = E^{\mathrm{atom}} - E^{\mathrm{v}}$ we also get [13]

$$E^{\mathrm{ion}} = \frac{1}{3}\left[T^{\mathrm{c}} + 2\left(V_{\mathrm{ne}}^{\mathrm{c}} + V_{\mathrm{ee}}^{\mathrm{cc}}\right)\right] . \tag{9}$$

E^{v} and E^{ion}, Eqs. (8) and (9), are calculated as part of our numerical work and are amenable to detailed comparisons with data taken from experimental ionization potentials [17]. Most of this work will be carried out with the help of CI wave functions, thus aiming at the best possible answers that are presently within reach. We will learn about the constraints imposed upon Eqs. (8) and (9) – namely, as regards the admissible values of N^{v} – and narrow down on the essence and physical justification of the concept underlying the core–valence partitioning of electronic charge advocated here for ground-state atoms and ions.

3 Outline of CI calculations

Our SDCI calculations were made using Hartree–Fock eigenfunctions

$$\phi_i^{\Omega} = \sum_{\mu}^{\mathcal{N}} C_{\mu i}^{\Omega} \chi_{\mu}^{l_\mu, m'_\mu}(r, \theta, \varphi) \tag{10}$$

where $\mathcal{N}$ is the dimension of the basis and Ω a spin index. These basis functions consist of a radial part, $R_\mu(r)$, and a real spherical harmonic angular part, i.e.,

$$\chi_{\mu}^{l_\mu, m'_\mu} = R_\mu(r) \times \mathcal{Y}_{l_\mu}^{m'_\mu}(\theta, \varphi) .$$

The CI many-electron wave function Ψ is written

$$\Psi = \sum_{s}^{\mathrm{CF}} c_s \Phi_s \tag{11}$$

where CF is the space of possible configuration functions. The subspace differing by only one spin-orbital from Φ_s is CF$'$ and CF$''$ spans the subspace differing from Φ_s by two spin-orbitals. The methods employed here are not size consistent.

Two-electron integrals

The calculation of the interelectronic repulsions, V_{ee}, involves the two-electron operator $|1/r_{12}|$ and thus the integral

$$\begin{aligned} I_{\mu\nu\sigma\lambda} &= \int\!\!\int\!\!\int\!\!\int\!\!\int\!\!\int \chi_\mu(1)\chi_\nu(1)\chi_\sigma(2)\chi_\lambda(2)\frac{1}{r_{12}}r_1^2r_2^2 \\ &\quad \times \sin\theta_1 \sin\theta_2 \,\mathrm{d}r_1\,\mathrm{d}r_2\,\mathrm{d}\theta_1\,\mathrm{d}\theta_2\,\mathrm{d}\varphi_1\,\mathrm{d}\varphi_2 \,. \end{aligned} \tag{12}$$

The integrals over φ and θ are carried out as usual, from 0 to 2π and from 0 to π, respectively. The integration limits for r_1 and r_2 depend on whether we calculate V_{ee}^{vv}, V_{ee}^{cc} or V_{ee}^{cv}. Any of these quantities is conveniently written

$$V_{ee} = J - K \tag{13}$$

using the familiar Coulomb and exchange integrals, J and K, respectively. Expansion of the SDCI wave function (11) using the ϕ_i^Ωs of Eq. (10) gives

$$J = \sum_{\mu,\nu,\sigma,\lambda}^{\mathscr{N}} I_{\mu\nu\sigma\lambda}\Gamma^{\mathrm{coul}}_{\mu\nu\sigma\lambda} \tag{14}$$

$$K = \sum_{\mu,\nu,\sigma,\lambda}^{\mathscr{N}} I_{\mu\nu\sigma\lambda}\Gamma^{\mathrm{exch}}_{\mu\nu\sigma\lambda} \,. \tag{15}$$

These equations hold for both SCF and SDCI wave functions. With the latter we obtain the following expressions for $\Gamma^{\mathrm{coul}}_{\mu\nu\sigma\lambda}$ and $\Gamma^{\mathrm{exch}}_{\mu\nu\sigma\lambda}$:

$$\begin{aligned} \Gamma^{\mathrm{coul}}_{\mu\nu\sigma\lambda} &= \sum_s^{\mathrm{CF}} c_s^2\,\Gamma^{\mathrm{coul}(s)}_{\mu\nu\sigma\lambda} + \sum_s^{\mathrm{CF}} c_s \sum_{t'<s}^{\mathrm{CF}'_s} c_{t'}\left(C^\Omega_{\mu m}C^\Omega_{\nu m'} + C^\Omega_{\mu m'}C^\Omega_{\nu m}\right) P^{s\cap t'}_{\sigma\lambda} \\ &\quad + \sum_s^{\mathrm{CF}} c_s \sum_{t''<s}^{\mathrm{CF}''_s} c_{t''}\left(C^\Omega_{\mu m}C^\Omega_{\nu m'}C^{\Omega'}_{\sigma n}C^{\Omega'}_{\lambda n'} + C^\Omega_{\mu m'}C^\Omega_{\nu m}C^{\Omega'}_{\sigma n'}C^{\Omega'}_{\lambda n}\right) \end{aligned} \tag{16}$$

$$\begin{aligned} \Gamma^{\mathrm{exch}}_{\mu\nu\sigma\lambda} &= \sum_s^{\mathrm{CF}} c_s^2\,\Gamma^{\mathrm{exch}(s)}_{\mu\nu\sigma\lambda} + \sum_s^{\mathrm{CF}} c_s \sum_{t'<s}^{\mathrm{CF}'_s} c_{t'}\left(C^\Omega_{\mu m}C^\Omega_{\lambda m'} + C^\Omega_{\mu m'}C^\Omega_{\lambda m}\right) P^{\Omega(s\cap t')}_{\sigma\nu} \\ &\quad + \sum_s^{\mathrm{CF}} c_s \sum_{t''<s}^{\mathrm{CF}''_s} c_{t''}\left(C^\Omega_{\mu m}C^\Omega_{\lambda m'}C^{\Omega'}_{\sigma n}C^{\Omega'}_{\nu n'} + C^\Omega_{\mu m'}C^\Omega_{\lambda m}C^{\Omega'}_{\sigma n'}C^{\Omega'}_{\nu n}\right)\delta_{\Omega\Omega'} \end{aligned} \tag{17}$$

where $\delta_{\Omega\Omega'}$ is the Kronecker delta. Only the first term on the right-hand side of Eqs. (16) and (17) survives in SCF calculations, with $c_0 = 1$. The Coulomb and exchange Γ functions appearing in the first terms on the right-hand side of (16) and (17) are

$$\Gamma^{\mathrm{coul}(s)}_{\mu\nu\sigma\lambda} = \frac{1}{2}\left[P^s_{\mu\nu}P^s_{\sigma\lambda} - (\mathrm{SIC})^s_{\mu\nu\sigma\lambda}\right] \tag{18}$$

$$\Gamma^{\mathrm{exch}(s)}_{\mu\nu\sigma\lambda} = \frac{1}{2}\left[\sum_\Omega P^{\Omega(s)}_{\mu\lambda}P^{\Omega(s)}_{\sigma\nu} - (\mathrm{SIC})^s_{\mu\nu\sigma\lambda}\right] \tag{19}$$

the self-interaction correction (SIC) being

$$(\mathrm{SIC})^{s}_{\mu\nu\sigma\lambda} = \sum_{\Omega}\sum_{i}^{\mathrm{occ}_s^{\Omega}} C^{\Omega}_{\mu i}C^{\Omega}_{\nu i}C^{\Omega}_{\sigma i}C^{\Omega}_{\lambda i} \,. \tag{20}$$

and where

$$P^{\Omega(s)}_{\mu\nu} = \sum_{i}^{\mathrm{occ}_s^{\Omega}} C^{\Omega}_{\mu i}C^{\Omega}_{\nu i} \tag{21}$$

$$P^{s}_{\mu\nu} = \sum_{\Omega}\sum_{i}^{\mathrm{occ}_s^{\Omega}} C^{\Omega}_{\mu i}C^{\Omega}_{\nu i} \,. \tag{22}$$

If s stands for a single excitation $i \rightarrow a$, we get

$$P^{\Omega(i\rightarrow a)}_{\mu\nu} = P^{\Omega}_{\mu\nu} - C^{\Omega}_{\mu i}C^{\Omega}_{\nu i} + C^{\Omega}_{\mu a}C^{\Omega}_{\nu a} \tag{23}$$

$$(\mathrm{SIC})^{i\rightarrow a}_{\mu\nu\sigma\lambda} = (\mathrm{SIC})^{\mathrm{HF}}_{\mu\nu\sigma\lambda} - C^{\Omega}_{\mu i}C^{\Omega}_{\nu i}C^{\Omega}_{\sigma i}C^{\Omega}_{\lambda i} + C^{\Omega}_{\mu a}C^{\Omega}_{\nu a}C^{\Omega}_{\sigma a}C^{\Omega}_{\lambda a} \tag{24}$$

where $(\mathrm{SIC})^{\mathrm{HF}}_{\mu\nu\sigma\lambda}$ is the Hartree–Fock self-interaction correction, namely,

$$(\mathrm{SIC})^{\mathrm{HF}}_{\mu\nu\sigma\lambda} = \sum_{\Omega}\sum_{i}^{\mathrm{occ}^{\Omega}} C^{\Omega}_{\mu i}C^{\Omega}_{\nu i}C^{\Omega}_{\sigma i}C^{\Omega}_{\lambda i} \,.$$

If, however, s stands for a double excitation $i \rightarrow a$ and $j \rightarrow b$, we have[4]

$$P^{\Omega(i,j\rightarrow a,b)}_{\mu\nu} = P^{\Omega(i\rightarrow a)}_{\mu\nu} - C^{\Omega}_{\mu j}C^{\Omega}_{\nu j} + C^{\Omega}_{\mu b}C^{\Omega}_{\nu b} \tag{25}$$

$$(\mathrm{SIC})^{i,j\rightarrow a,b}_{\mu\nu\sigma\lambda} = (\mathrm{SIC})^{i\rightarrow a}_{\mu\nu\sigma\lambda} - C^{\Omega'}_{\mu j}C^{\Omega'}_{\nu j}C^{\Omega'}_{\sigma j}C^{\Omega'}_{\lambda j} + C^{\Omega'}_{\mu b}C^{\Omega'}_{\nu b}C^{\Omega'}_{\sigma b}C^{\Omega'}_{\lambda b} \,. \tag{26}$$

Finally, the $P^{s\cap t'}$ terms of Eqs. (16) and (17) are defined by

$$\begin{aligned} P^{s\cap t'}_{\mu\nu} &= \sum_{\Omega}\sum_{i}^{\mathrm{occ}^{\Omega}_{s\cap t'}} C^{\Omega}_{\mu i}C^{\Omega}_{\nu i} \\ &= P^{s}_{\mu\nu} - C^{\Omega}_{\mu m}C^{\Omega}_{\nu m} \,. \end{aligned} \tag{27}$$

Equations (16)–(27) indicate how we can use the reduced second-order density matrix to get the required Coulomb and exchange integrals from Eqs. (14) and (15), using also the integral (12) with the appropriate limits of integration indicated in (3)–(5). Note that (15) defines exchange and reduces to the usual Hartree–Fock exchange with the use of SCF wave functions. The self-interaction corrections (20) which cancel in common evaluations of $J - K$ are needed here to get the K^{cv} core-valence exchange.

---

[4] In Eq. (25) we have tacitly assumed that both excitations, $i \rightarrow a$ and $j \rightarrow b$, are of the same spin. If this should not be so, one writes two equations (23), one for each excitation. No such spin restriction occurs in (26).

One-electron integrals

The reduced first-order density matrix is involved in the evaluation of one-electron properties, where $\hat{O}$ is a one-electron operator, say, $\hat{T}$, $\hat{V}_{\text{ne}}$ or $\hat{1}$ for the electron density. The integral

$$O = \int \Psi^* \hat{O} \Psi \, \mathrm{d}\tau \tag{28}$$

gives the value of that property. The integrations over θ and φ are carried out as usual between 0 and π and between 0 and 2π, respectively. If the integrals over r are taken between 0 and r_{b} we obtain the core-contribution to O, while integrals spanning the range from r_{b} to ∞ represent the contribution of the valence region. With this understanding, we obtain from the SDCI wave function given by (11) that

$$O = \sum_{\mu}^{\mathcal{N}} \sum_{\nu \leq \mu} P_{\mu\nu} O_{\mu\nu} \tag{29}$$

where

$$P_{\mu\nu} = \sum_{s}^{\text{CF}} c_s^2 P_{\mu\nu}^s + \sum_{s}^{\text{CF}} c_s \sum_{t'<s}^{\text{CF}'_s} c_{t'} \left(C_{\mu m}^{\Omega} C_{\nu m'}^{\Omega} + C_{\mu m'}^{\Omega} C_{\nu m}^{\Omega} \right) \tag{30}$$

with $P_{\mu\nu}^s$ as given by Eq. (22). Moreover, we have for single excitations $i \to a$

$$P_{\mu\nu}^{i \to a} = P_{\mu\nu}^{\text{HF}} - C_{\mu i}^{\Omega} C_{\nu i}^{\Omega} + C_{\mu a}^{\Omega} C_{\nu a}^{\Omega} \tag{31}$$

where $P_{\mu\nu}^{\text{HF}}$ stands for the Hartree–Fock SCF value. Similarly, for double excitations $i \to a$ and $j \to b$ we write

$$P_{\mu\nu}^{i,j \to a,b} = P_{\mu\nu}^{i \to a} - C_{\mu j}^{\Omega'} C_{\nu j}^{\Omega'} + C_{\mu b}^{\Omega'} C_{\nu b}^{\Omega'} \, . \tag{32}$$

This concludes the description of the required one-electron integrals.

Comments

The merit of Eqs. (16) and (17) met in our description of the second-order density matrix is in the fact that they express $\Gamma_{\mu\nu\sigma\lambda}^{\text{coul}}$ and $\Gamma_{\mu\nu\sigma\lambda}^{\text{exch}}$ in an explicit manner. Though their applications lead to the correct numerical results, it appears that in this form their programming does not turn to our advantage. An efficient file maintenance of two-electron integrals is of utmost importance and we must also consider that our analysis requires separate calculations of the Coulomb and exchange integrals. Hence, rather than using the methods proposed by Raffenetti [18] which are most useful in direct calculations of the difference $(J - K)$, we implemented a segregation of two-electron integrals in the basis of atomic orbitals similar to that described by Billingsley [19], by taking full advantage of their symmetry properties. Moreover, important gains are made with the use of well-known standard methods [20] of 4-index transformations to reduce the number of operations required to cover all μ, ν, σ and λ indices. Generally speaking, standard methods were applied wherever possible but with our attention kept on the one- and two-electron integrals which – in contrast with the usual situation – are made only for specified core and valence regions in real space. Computational details may be found in ref. [21].

4 Basis functions

The 6–311G* basis developed by Pople and coworkers [22, 23] – the smallest one used in our calculations – was selected as a convenient reference. It was used for all atoms from Li through Ar. For the first-row atoms we have also used van Duijneveldt's $(13s\,8p)$ basis [24] augmented with d and f functions taken from [25]. 'Atomic Natural Orbital' (ANO) bases [26], namely [27]

$$\begin{array}{rcll} \mathrm{ANO}(10s\,4p\,3d) & \rightarrow & \mathrm{ANO}[6s\,4p\,3d] & (\mathrm{Li,\ Be,\ Be^+}) \\ \mathrm{ANO}(10s\,6p\,3d) & \rightarrow & \mathrm{ANO}[7s\,6p\,3d] & (\mathrm{B-Ne\ and\ ions}) \\ \mathrm{ANO}(14s\,9p\,4d\,3f) & \rightarrow & \mathrm{ANO}[5s\,4p\,3d\,2f] & (\mathrm{Li-Ne\ and\ ions}) \\ \mathrm{ANO}(17s\,12p\,5d\,4f) & \rightarrow & \mathrm{ANO}[5s\,4p\,3d\,2f] & (\mathrm{Na-Ar}) \end{array}$$

were used in comparisons between the first-row atoms and their positive and negative ions and for Na–Ar. The coefficients, c_s, of Eq. (11) were calculated with the GAUSSIAN 90 program [23].

5 Results

Consideration of our core–valence electron partitioning in ground state atoms and ions raises the question about the energy of the outer electrons that could be measured by the energy required to remove them. This entails the notion of integer numbers of electrons in both the core and valence regions because electrons cannot be removed in fractional amounts. The valence-region energy formula advocated here, Eq. (8), is examined on this basis. The selection of a physically meaningful core–valence partitioning thus revolves about the selection of the appropriate integer numbers of core and valence electrons associated with their respective spatial regions. Numerical results are here to guide us.

To begin with, let us consider the minima of the radial distribution function, $D(r) = 4\pi r^2 \rho(r)$, and examine whether this criterion permits a valid separation into core and valence regions with integer electron populations. SCF analyses [9] using the near-Hartree–Fock wave functions of Clementi [28] indicate that the numbers of electrons found in the inner shell extending up to the minimum of the radial distribution function $D(r)$ amount to $N^{\mathrm{c}} = 2.054$ e (Be), 2.131 (C), 2.186 (O), 2.199 (F) and 2.205 electron (Ne). Our SDCI results, obtained with the $(13s\,8p\,2d\,1f)$ basis, are virtually the same, with N^{c} values of 2.059 (Be), 2.134 (C), 2.189 (O), 2.203 (F) and 2.206 electron (Ne). The results of Smith et al. [29] bearing on the boundaries in position space that enclose the exact electron number given by the Aufbau principle surely support the idea of 'physical' shells compatible with that principle. The maxima of $D(r)$, on the other hand, also appear to be topological features indicative of shells: their positions correlate well with the shell radii from the Bohr–Schrödinger theory of an atom [30]. The critical points in $\nabla^2\rho(r)$, in contrast, though highly indicative of atomic shells in a qualitative sense, are not suitable for defining meaningful shell boundaries [31]. So, on the basis of these results, we shall keep in mind that the radial distribution function offers a vivid pictorial reference suggesting an involvement of the electronic shell structure in the separation of core and valence regions in atoms, but also that one should definitively not attempt to carry this picture too far.

Hence we direct our attention to the core–valence exchange terms or, more precisely, to K^{cv}, the sum of all exchange integrals between the N^{c} core and the N^{v}

valence electrons. K^{cv} depends on the radius selected for the inner core region and so does N^c, of course. Thus we can represent K^{cv} as a function of N^c. Two examples are offered in Figs. 1 and 2: the results for neon are typical for first-row atoms, those of argon are representative for second-row elements: for the first-row elements, $K^{cv} \approx 0$ for $N^c = 2$ e whereas, for the second-row atoms, $K^{cv} \approx 0$ for $N^c = 2$ and $N^c = 10$ e[5]. Table 1 examines this point a little more in detail. For comparison, we offer the SCF results obtained with the near-Hartree–Fock wave functions of Clementi and Roetti [32] and the SDCI results obtained with the 6–311G*, ANO and ($13s\,8p\,2d\,1f$) bases. It is clear that the K^{cv} integrals closely approach zero when $N^c = 2$ and $N^c = 10$ e. To appraise the significance of this result, we must compare it with the total exchange, K^{total}, calculated for the entire atom. K^{total} is small, of course, for lithium, 0.0220 au, but increases rapidly with the size of the atom: 0.0587 (Be), 0.6396 (C), 1.2801 (O) and 2.3758 au (Ne) in the ($13s\,8p\,2d\,1f$) basis, with CI. Briefly, K^{total} is certainly sufficiently large to brand K^{cv} as a negligible quantity, in comparison. Surely, this argument applies *a fortiori* also to the second-row elements where the total exchange integrals are still larger, up to ~ 7.82 au for argon.

Table 1. K^{cv} exchange energies, atomic units

Atom	N^c	near-HF SCF[a]	6–311G*	ANO[b]	($13s\,8p\,2d\,1f$)
Li	2	−0.0027	−0.0024	−0.0021	−0.0017
Be	2	−0.0148	−0.0136	−0.0130	−0.0127
B	2	−0.0254	−0.0229	−0.0215	−0.0116
C	2	−0.0347	−0.0303	−0.0282	−0.0155
N	2	−0.0404	−0.0327	−0.0308	−0.0167
O	2	−0.0471	−0.0401	−0.0363	−0.0206
F	2	−0.0488	−0.0397	−0.0363	−0.0142
Ne	2	−0.0449	−0.0297	−0.0019	−0.0003
Na	10	0.0050	0.0064	0.0053	
Mg	10	0.0118	0.0128	0.0124	
Al	10	0.0158	0.0183	0.0174	
Si	10	0.0171	0.0211	0.0204	
P	10	0.0138	0.0182	0.0189	
S	10	0.0019	0.0275	0.0077	
Cl	10	−0.0186	−0.0111	−0.0098	
Ar	10	−0.0450	−0.0075	−0.0358	

[a] Calculated with Slater bases near the HF limit given by Clementi and Roetti [32]

[b] Contracted ANO($10s\,6p\,3d$) $\rightarrow$ ANO[$7s\,6p\,3d$] bases were used for the series B–Ne and ANO($17s\,12p\,5d\,4f$) $\rightarrow$ ANO[$5s\,4p\,3d\,2f$] for Na–Ar. For Li and Be we used the ANO($10s\,4p\,3d$) $\rightarrow$ ANO[$6s\,4p\,3d$] basis sets [27]

Yet it is difficult to ascertain conclusively whether small differences of this sort between K^{cv} and 0 stem from the incompleteness of our CI wave functions or whether they are (at least partly) genuine. So, while small departures from 0 cannot be entirely ruled out for K^{cv} in situations where N^c is *exactly* 2 or 10 e, depending on what atom (or ion) we are talking about, it seems fair to claim that the criterion resting on vanishing core–valence exchange integrals clearly establishes the identity of the

---

[5] SCF results obtained with near-Hartree–Fock wave functions [32] indicate similar patterns for Ti, Cr, Fe, Ni, Zn, Ge, Se and Kr, namely 'almost' vanishing K^{cv} integrals for $N^c = 2$ and $N^c = 10$ e. A third point exists for krypton, for $N^c = 28$ e, where K^{cv} reaches a minimum [13].

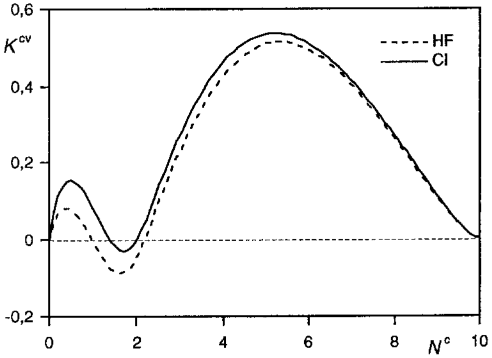

Fig. 1. Neon. K^{cv} vs. N^c (au), from ($13s\,8p\,2d\,1f$) SCF and SDCI calculations

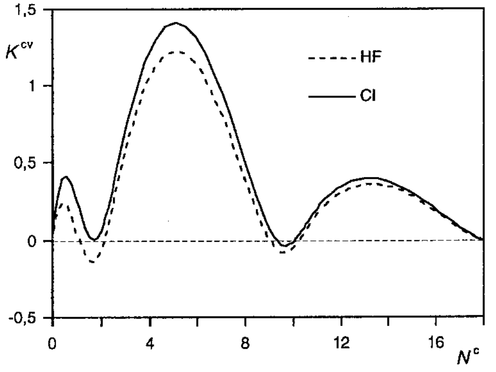

Fig. 2. Argon. K^{cv} vs. N^c (au), from 6–311G* SCF and SDCI calculations

Table 2. Selected kinetic and potential valence-region energies of C, F and Ne, au[a]

Atom	N^c	V_{ee}^{vv}	V_{ee}^{cv}	V_{ne}^{v}	T^v	E^v	
						Calcd.	Exptl.[b]
C	1	6.4902	4.5741	−36.1302	4.2833	−15.283	−19.849
	2	2.9648	5.7358	−18.0060	2.4073	−5.401	−5.440
	3	1.3611	4.6819	−10.4404	1.1533	−2.547	−3.070
F	1	26.0057	10.9725	−119.1931	20.9946	−47.812	−59.268
	2	16.8157	16.1570	−76.1107	13.4101	−24.289	−24.212
	3	10.9430	16.9484	−54.3146	8.7695	−14.692	−17.406
	4	6.8605	16.0133	−39.6055	4.6120	−9.617	−11.631
Ne	1	37.0049	13.7487	−163.0250	30.8793	−64.554	−78.991
	2	25.3052	20.8567	−109.1037	20.3326	−35.184	−35.045
	3	17.4010	22.8145	−80.7045	13.8571	−22.374	−26.258
	4	11.6797	22.5013	−61.1987	8.0261	−15.336	−18.641
	5	7.3925	20.6915	−45.6632	4.2586	−10.300	−12.837

[a] SDCI results in the ($13s\,8p\,2d\,1f$) basis

[b] Taken as the appropriate sum of ionization potentials [17], with a change in sign, using 1 au = 27.2106 eV

Table 3. Kinetic and potential energies of the first-row atoms ($N^c = 2$) and the second-row atoms ($N^c = 10$ e), atomic units[a]

Atom	V_{ee}^{cc}	V_{ee}^{vv}	V_{ee}^{cv}	V_{ne}^{c}	V_{ne}^{v}	T^c	T^v
Li	1.6174	0.0081	0.5784	−16.2393	−0.9096	7.4324	0.0389
Be	2.3332	0.3032	1.7515	−30.0516	−3.6493	14.3719	0.2829
B	3.0719	1.1829	3.4356	−48.0011	−8.9679	23.6486	0.9896
C	3.8478	2.9648	5.7358	−70.1906	−18.0060	35.4146	2.4073
N	4.6542	5.9548	8.6533	−96.6515	−31.7282	49.7337	4.8191
O	5.4836	10.4663	12.0894	−127.4387	−50.6457	66.6739	8.3430
F	6.3368	16.8157	16.1570	−162.5434	−76.1107	86.2549	13.4101
Ne	7.2116	25.3052	20.8567	−201.9912	−109.1037	108.5209	20.3326
Na	63.0164	0.0174	2.6155	−386.4863	−2.9412	161.8040	−0.0022
Mg	72.4138	0.2761	6.8239	−470.5155	−8.3516	199.4997	0.0931
Al	81.7977	0.8802	11.8548	−562.8752	−15.6824	241.5790	0.4109
Si	91.2371	2.0036	18.2746	−663.5598	−25.9963	288.0276	0.9874
P	100.7850	3.7707	25.9897	−772.8109	−39.5719	339.0543	1.8831
S	110.4249	6.3891	34.7978	−890.6209	−56.4650	394.6717	3.0926
Cl	120.2331	9.9433	44.9168	−1016.8571	−77.3888	454.7887	4.7198
Ar	130.0772	14.6332	56.4206	−1152.1142	−102.8540	519.9928	6.8324

[a] SDCI results obtained with the ($13s\,8p\,2d\,1f$) basis for Li–Ne and with the 6–311G* basis for the series Na–Ar

core and valence regions: $N^c = 2$ (or $N^c = 10$) e are the only acceptable solutions in applications of Eqs. (8) and (9) in spite of the possibly approximate nature of our identification.

This analysis carries a strong conjecture regarding the uniqueness attached to the constraint $K^{cv} = 0$, namely as concerns the validity of our Eqs. (8) and (9). Typical examples, carbon, fluorine and neon, nicely illustrate this point. Table 2 reports their kinetic and potential valence-region energy components for $N^c = 1, 2, 3, \ldots$ electron and the corresponding E^v values given by Eq. (8): experimental data unmistakably pick $N^c = 2$ e as the correct solution. Similar tests pick both $N^c = 2$ and $N^c = 10$ e for the second-row elements. These constraints are henceforth incorporated into the presentation of our results.

Table 3 reports the relevant kinetic and potential core and valence energy components of the first- and second-row atoms, for use in Eqs. (8) and (9). These are SDCI results obtained with the ($13s\,8p\,2d\,1f$) basis taking $N^c = 2$ e for the atoms Li–Ne and with Pople's 6–311G* basis for the second-row, with $N^c = 10$ e. Similar SDCI results were also obtained for the first-row elements using the 6–311G* basis. Positive and negative ions, A^+ and A^-, respectively, as well as their parent first-row ground state atoms are examined in Table 4 with the help of ANO wave functions. The results obtained for the neutral atoms turn out to be close to those deduced with the 6–311G* basis. The merits of the density matrix averaged atomic natural orbital (ANO) basis sets [26] lie, in this particular context, in their construction [27, 33] which includes by design functions that describe the deformation of the atomic orbitals when cations and anions are formed. These sets are, indeed, known to perform well at the correlated level for the atomic ionization potentials and electron affinities [27] – a circumstance that motivated our selection of ANO bases in this instance.

The E^v and E^{ion} energies are given in Tables 5 to 7. They vividly illustrate the general validity of our master formulas, Eqs. (8) and (9). It is of particular interest

Table 4. Kinetic and potential energies of selected first-row atoms and ions, A^-, A and A^+, calculated for $N^c=2$ electron using ANO (Atomic Natural Orbital) basis sets[a], atomic units

Atom or Ion	V_{ee}^{cc}	V_{ee}^{vv}	V_{ee}^{cv}	V_{ne}^{c}	V_{ne}^{v}	T^c	T^v
Li	1.6604	0.0080	0.5769	−16.2266	−0.9059	7.3991	0.0388
Be^+	2.3359	0.0183	0.9382	−29.8674	−1.9916	14.1461	0.1244
Be	2.3715	0.3009	1.7488	−30.0250	−3.6422	14.3277	0.2830
B^+	3.0517	0.4506	2.4905	−48.1296	−6.5205	23.6804	0.6425
B	3.0757	1.1824	3.4308	−47.9861	−8.9555	23.6274	0.9906
B^-	3.0742	1.9222	3.9853	−47.8931	−10.3505	23.5416	1.0827
C^+	3.8308	1.6554	4.6193	−70.3472	−14.5579	35.4638	1.9272
C	3.8513	2.9652	5.7284	−70.1708	−17.9828	35.3696	2.4224
C^-	3.8510	4.2435	6.4621	−70.0409	−20.2020	35.2478	2.5840
N^+	4.6395	3.9288	7.3666	−96.8377	−27.1135	49.8039	4.1905
N	4.6572	5.9570	8.6440	−96.6275	−31.6942	49.6647	4.8489
N^-	4.6568	7.7554	9.3981	−96.5146	−34.3279	49.5478	4.9634
O^+	5.4741	7.5795	10.7374	−127.6279	−45.1664	66.7252	7.7560
O	5.4863	10.4670	12.0720	−127.4102	−50.5717	66.5554	8.3989
O^-	5.4861	13.0336	13.0013	−127.2674	−54.2885	66.4056	8.5942
F^+	6.3274	12.9919	14.6403	−162.7498	−69.1969	86.2958	12.6702
F	6.3389	16.8137	16.1354	−162.5081	−76.0065	86.0961	13.4855
F^-	6.3392	20.2600	17.2308	−162.3354	−80.9447	85.9143	13.7849
Ne^+	7.2020	20.4025	19.1743	−202.2133	−100.5849	108.5670	19.4064
Ne	7.2128	25.2949	20.8303	−201.9451	−108.9621	108.3344	20.4093

[a] The atoms B–Ne and their ions were calculated with the ANO[7*s* 6*p* 3*d*] basis [27]. For Li, Be and Be^+, however, we used the ANO(10*s* 4*p* 3*d*) →ANO[6*s* 4*p* 3*d*] basis given in [27]

Table 5. Comparison between the calculated[a] and experimental energies of the valence electrons, E^v, and of the 2-electron ions, E^{ion}, atomic units

Atom	6–311G*		(13*s* 8*p* 2*d* 1*f*)		Exptl.[b]	
	E^v	E^{ion}	E^v	E^{ion}	E^v	E^{ion}
Li	− 0.201	− 7.242	− 0.202	− 7.270	− 0.198	− 7.280
Be	− 0.965	− 13.662	− 0.969	− 13.688	− 1.012	− 13.657
B	− 2.560	− 22.047	− 2.570	− 22.070	− 2.623	− 22.035
C	− 5.381	− 32.404	− 5.401	− 32.424	− 5.440	− 32.416
N	− 9.774	− 44.735	− 9.807	− 44.754	− 9.810	− 44.802
O	− 15.893	− 59.056	− 15.946	− 59.079	− 15.916	− 59.194
F	− 24.219	− 75.358	− 24.289	− 75.386	− 24.212	− 75.595
Ne	− 35.098	− 93.642	− 35.184	− 93.679	− 35.045	− 94.006

[a] Results obtained from Eqs. (8) and (9) for E^v and E^{ion}, respectively, using the input data given in Table 3 for van Duijneveldt's (13*s* 8*p* 2*d* 1*f*) basis (with *d* and *f* functions from [25]) and similar data (not reported here) deduced with the help of Pople's 6–311G* basis set

[b] Taken as the appropriate sums of experimental ionization potentials [17], with a change in sign, using the conversion factor 1 atomic unit = 27.2106 eV

Table 6. Comparison between the calculated and experimental energies of the valence electrons, E^{v}, and of the 2-electron ions, E^{ion}, of selected first-row atoms and ions A^-, A and A^+, using contracted ANO basis sets, atomic units

Atom/Ion	ANO[7*s* 6*p* 3*d*][a]		ANO[5*s* 4*p* 3*d* 2*f*]		Experimental[b]	
	E^{v}	E^{ion}	E^{v}	E^{ion}	E^{v}	E^{ion}
Li	− 0.201	− 7.244	− 0.201	− 7.234	− 0.198	− 7.280
Be^+	− 0.649	− 13.639	− 0.647	− 13.625	− 0.669	− 13.657
Be	− 0.967	− 13.660	− 0.969	− 13.648	− 1.012	
B^+	− 2.172	− 22.158	− 2.172	− 22.124	− 2.318	− 22.035
B	− 2.565	− 22.064	− 2.566	− 22.030	− 2.623	
B^-	− 2.601	− 22.032	− 2.602	− 21.997	− 2.634	
C^+	− 4.880	− 32.523	− 4.883	− 32.484	− 5.026	− 32.416
C	− 5.385	− 32.423	− 5.397	− 32.382	− 5.440	
C^-	− 5.470	− 32.377	− 5.480	− 32.338	− 5.486	
N^+	− 9.149	− 44.864	− 9.156	− 44.820	− 9.276	− 44.802
N	− 9.779	− 44.759	− 9.801	− 44.711	− 9.810	
N^-	− 9.795	− 44.723	− 9.817	− 44.681	− 9.805	
O^+	− 15.314	− 59.194	− 15.340	− 59.134	− 15.416	− 59.194
O	− 15.889	− 59.098	− 15.941	− 59.033	− 15.916	
O^-	− 15.971	− 59.052	− 16.019	− 58.994	− 15.970	
F^+	− 23.486	− 75.516	− 23.535	− 75.446	− 23.572	− 75.595
F	− 24.210	− 75.414	− 24.286	− 75.339	− 24.212	
F^-	− 24.374	− 75.359	− 24.438	− 75.339	− 24.339	
Ne^+	− 34.203	− 93.819	− 34.309	− 93.724	− 34.252	− 94.006
Ne	− 35.088	− 93.710	− 35.179	− 93.635	− 35.045	

[a] For Li, Be and Be^+, however, we used the ANO[6*s* 4*p* 3*d*] basis recommended in [27]

[b] Taken as minus the appropriate sums of ionization potentials [17] and electron affinities given in [34] for C, [35] for N, [36] for O, and in [37] for F, using the value (0.3 eV) calculated by Clementi and McLean [38] for boron

that this holds for *integer* numbers of electrons, N^{v} and N^{c}, assigned to the individual valence and core atomic regions: E^{v} and E^{ion} are observables.

While the relatively modest 6–311G* set gives acceptable results for the first-row elements, things understandably deteriorate in the second row, particularly for the larger atoms. Our results are just ‘fair’ for atoms larger than aluminium but none the less sufficiently clear to support the basic tenets underlying Eqs. (8) and (9) and our criterion defining core and valence regions. Of course, part of the problem is with the relatively modest size of the basis sets which were employed – the ANO[5*s* 4*p* 3*d* 2*f*] results are not significantly different from those given by the 6–311G* basis – but relativistic effects and size-consistency certainly ought to be taken into consideration at this point. Relativistic corrections to the total energy are always negative for the ground-state configurations of atoms. In Datta’s calculations [39] they amount to −0.01634 au for carbon, −0.05577 au for oxygen and −0.14482 au for neon, to cite a few examples. These corrections grow rapidly with the size of the atoms, e.g., −0.409 (Al), −0.771 (P), −1.024 (S), −1.339 (Cl) and −1.722 hartree for argon [40] and become numerically more important than possible improvements in CI calculations – a fact well worth remembering in the assessment of energy results like those presented here for the heavier atoms.

Our formula for the valence-region energy in real space, $E^{\mathrm{v}} = \frac{1}{3}(T^{\mathrm{v}} + 2V^{\mathrm{v}})$, measures the energy required for the actual removal of the electrons which are com-

Table 7. Comparison between the calculated and experimental energies of the valence electrons, E^{v}, and of the corresponding ions, E^{ion}, of the second-row atoms, assuming either N^{c} = 2 e or N^{c} = 10 electron, atomic units

Atom	N^{c}	6–311G*		ANO[5*s* 4*p* 3*d* 2*f*]		Experimental[a]	
		E^{v}	E^{ion}	E^{v}	E^{ion}	E^{v}	E^{ion}
Na	10	−0.206	−161.712	−0.204	−161.625	−0.189	−162.240
	2	−47.923	−113.995	−47.780	−114.049	−47.997	−114.432
Mg	10	−0.803	−198.901	−0.809	−198.796	−0.834	−199.477
	2	−63.218	−136.486	−63.064	−136.540	−63.436	−136.874
Al	10	−1.828	−240.192	−1.832	−240.069	−1.957	−240.756
	2	−80.999	−161.021	−80.838	−161.063	−81.376	−161.337
Si	10	−3.483	−285.539	−3.489	−285.403	−3.790	−286.079
	2	−101.447	−187.575	−101.275	−187.617	−102.046	−187.823
P	10	−5.913	−334.999	−5.924	−334.852	−6.497	−335.451
	2	−124.749	−216.163	−124.570	−216.206	−125.609	−216.339
S	10	−9.155	−388.573	−9.186	−388.409	−10.163	−388.874
	2	−150.938	−246.790	−150.761	−246.834	−152.150	−246.887
Cl	10	−13.446	−446.153	−13.489	−446.114	−15.026	−446.356
	2	−180.137	−279.462	−180.115	−279.489	−181.910	−279.473
Ar	10	−18.923	−508.027	−18.977	−507.985	−21.232	−507.882
	2	−212.819	−314.131	−212.789	−314.173	−215.013	−314.102

[a] Taken as minus the appropriate sums of experimental ionization potentials [17]

monly known as ‘valence electrons’ in the familiar shell model. This energy takes the concurrent core relaxation into account. The simple sum of the kinetic and potential energies of the N^{v} electrons found outside the boundary defined by r_{b}, i.e., $T^{\mathrm{v}} + V^{\mathrm{v}}$, in contrast, describes a hypothetical ionization that would simply skim off the electronic charge found in the outer region without allowing any relaxation. The difference beween $T^{\mathrm{v}} + V^{\mathrm{v}}$ and E^{v}, i.e., $\Delta E_{\mathrm{relax}} = \frac{1}{3}(2T^{\mathrm{v}} + V^{\mathrm{v}})$, measures the relaxation accompanying the actual removal of the valence electrons from a ground-state neutral atom or its ions. The sums $(T^{\mathrm{v}} + V^{\mathrm{v}})$ – which are easily deduced from Tables 3 and 4 – differ significantly from the corresponding E^{v} energies and the relaxation is important, e.g., $\Delta E_{\mathrm{relax}} = -1.497$ au for carbon, -3.801 au for oxygen and -7.426 au for neon. Surely, the energy represented by $(T^{\mathrm{v}} + V^{\mathrm{v}})$, where T^{v} and V^{v} are given in real space, should not be mistaken for a *physical* valence-region energy, i.e., an energy that could be actually measured. Only E^{v} and E^{ion} are physical: their nature is convincingly demonstrated by the experimental data offered for comparison in Tables 5–7.

6 Conclusions

The formula giving the valence-region energy in *real space*, $E^{\mathrm{v}} = \frac{1}{3}(T^{\mathrm{v}} + 2V^{\mathrm{v}})$, sharply differs from that applicable in the *orbital space* where the valence energy is just the simple sum of the pertinent electronic kinetic and potential energies. The relevant kinetic and potential energies are evidently not the same in the orbital and in real space. They proceed from integrations over the full coordinate space in the former, contrasting with integrals spanning appropriate portions of the total space for use in

$E^v = \frac{1}{3}(T^v + 2V^v)$. Yet, under well specified conditions one gets the same results in both approaches.

In the orbital space, the core-valence separation of electrons is made with reference to some property (orbital energy or principal quantum number) but in real space this segregation is made solely with reference to the admissible number, N^c, of core electrons. The uniqueness of this partitioning in real space (which carries over in orbital space where the valence energies are the same) goes back to E^v which accepts only discrete solutions, namely with $N^c = 2$ e for the first-row elements or $N^c = 2$ and 10 e for the second row, i.e., anytime the exchange integrals between the core- and the valence-region electrons are down to zero. For any other N^c, large discrepancies are found between the calculated E^v values and the corresponding ionization potential sums.

We conclude that the agreement between E^v and the sum of the ionization potentials is significant and that it provides strong support for the contention that physically meaningful cores are defined in real space by taking $N^c = 2$ e for the first-row atoms and $N^c = 2$ or 10 e for the larger elements.

Acknowledgement. We express our gratitude to Drs. Kristine Pierloot, Birgit Dumez, Per–Olof Widmark and Björn O. Roos for their help with the ANO bases and thank Professor Vincenzo Barone and Dr. Mark E. Casida for most helpful comments and suggestions. The financial support offered by the Natural Sciences and Engineering Research Council of Canada and by the FCAR, Québec, is gratefully acknowledged.

References

1. Dixon RN, Robertson IL (1978) Specialist Periodical Reports, Theoretical Chemistry, vol 3, chap 4, The Chemical Society, London
2. Delgado–Barrio G, Prat RF (1975) Phys Rev A 12: 2288
3. Sjoberg P, Murray JS, Brinck T, Politzer P (1990) Can J Chem 68: 1440
4. Politzer P, Murray JS, Grice ME (1993) Charge Capacities and Shell Structures of Atoms, Structure and Bonding 80: 101, Springer-Verlag, Berlin Heidelberg
5. Politzer P, Murray JS, Grice ME, Brinck T, Ranganathan (1991) J Chem Phys 95: 6699
6. Politzer P (1980) J Chem Phys 72: 3027
7. Sen KD, Gayatri TV, Krishnaveni R, Kakkar M, Toufar H, Janssens GOA, Baekelandt BG, Schoonheydt RA, Mortier WJ (1995) Int J Quantum Chem 56: 399
8. Wang W–P, Parr RG (1977) Phys Rev A 16: 891
9. Politzer P, Parr RG (1976) J Chem Phys 64: 4634
10. Weinstein H, Politzer P, Srebrenik S (1975) Theor Chim Acta 38: 159
11. Fliszár S, Desmarais N, Dancausse G (1992) Can J Chem 70: 537
12. Desmarais N, Dancausse G, Fliszár S (1993) Can J Chem 71: 175
13. Fliszár S (1994) Atoms, Chemical Bonds and Bond Dissociation Energies (Lecture Notes in Chemistry 63) Springer-Verlag, Heidelberg Berlin
14. Goodisman J (1970) Phys Rev A 2: 1193; (1972) Theor Chim Acta 24: 1
15. Gombás P (1949) Die Statistische Theorie des Atoms and ihre Anwendungen, Springer-Verlag, Wien
16. Politzer P, Daiker KC (1973) Chem Phys Lett 20: 309
17. Moore CE (1970) Natl Stand Ref Data Ser (US Natl Bur Stand) 34
18. Raffenetti RC (1973) Chem Phys Lett 20: 335
19. Billingsley FP (1972) Int J Quantum Chem 6: 617
20. Wilson S (1987) Methods in Computational Chemistry, v 1, Electron Correlation in Atoms and Molecules (Wilson S, ed), p 251, Plenum Press, New York, London
21. Desmarais N (1995) PhD Thesis, Département de Chimie, Université de Montréal, Montréal, Qc, Canada
22. Krishnan R, Binkley JS, Seeger R, Pople JA (1980) J Chem Phys 72: 650

23. GAUSSIAN 90 Revision J (1990), Frisch MJ, Head–Gordon M, Trucks GW, Foresman JB, Schlegel HB, Raghavachari K, Robb M, Binkley JS, Gonzalez C, Defrees DJ, Fox DJ, Whiteside RA, Seeger R, Melius CF, Baker J, Martin RL, Kahn LR, Stewart JJP, Topiol S, Pople JA, Gaussian, Inc., Pittsburgh PA
24. van Duijneveldt FB (1971) Technical Report RJ 945, IBM Research Laboratories, San Jose CA
25. Frisch MJ, Pople JA, Binkley JS (1984) J Chem Phys 80: 3265
26. Almlöf J, Taylor PR (1987) J Chem Phys 86: 4070
27. Pierloot K, Dumez B, Widmark P-O, Roos BO (1995) Theor Chim Acta 90: 87
28. Clementi E (1965) Tables of Atomic Functions, IBM Corp., San Jose CA
29. Schmider H, Sagar RP, Smith Jr VH (1992) Can J Chem 70: 506
30. Simas AM, Sagar RP, Ku ACT, Smith Jr VH (1988) Can J Chem 66: 1923
31. Schmider H, Sagar RP, Smith Jr VH (1991) J Chem Phys 94: 8627
32. Clementi E, Roetti C (1974) At Data Nucl Data Tables 14: 179
33. Widmark P-O, Malmqvist P-Å, Roos BO (1990) Theor Chim Acta 77: 291; Widmark P-O, Persson BJ, Roos BO (1991) Theor Chim Acta 79: 419
34. Seman ML, Branscomb LM (1962) Phys Rev 125: 1602
35. Sambe H, Felton RH (1976) Chem Phys 13: 299
36. Branscomb LM, Burch DS, Smith SJ, Geltman S (1963) Phys Rev 111: 504
37. Berry RS, Reimann CW (1963) J Chem Phys 38: 1540
38. Clementi E, McLean AD (1964) Phys Rev A 133: 419
39. Datta SN (1995) Int J Quantum Chem 56: 91
40. Desclaux JP (1973) At Data Nucl Data Tables 12: 311

This article was processed by the author using the LaTeX style file *pljour1* from Springer-Verlag.