

# Core and valence regions of molecules

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Received: 21 August 1996 / Accepted: 14 November 1996

**Abstract.** In real space, the partitioning of a molecule into valence and core regions is rooted in the picture of ‘valence electrons’ in the field of ‘effective cores’ consisting of nuclei partially shielded by inner-shell ‘core’ electrons. The appropriate valence kinetic and potential energies,  $T^v$  and  $V^v$ , respectively, are obtained by subtracting the pertinent parts associated with the cores from the corresponding conventional total  $T$  and  $V$  energies but, far from  $T^v + V^v$ , the physically correct valence-region energy is  $E^v = \frac{1}{3}(T^v + 2V^v)$ . This result differs markedly from  $T^v + V^v$  because  $E^v$ ,  $T^v$  and  $V^v$  do not obey the virial theorem.

**Key words:** Molecules – Core-valence partitioning – Valence energy

## 1 Introduction

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 surely offers a direct, vivid way of separating core and valence electrons in real space [1]–[4]. The number of core electrons,  $N^c$ , is then

$$N^c = 4\pi \int_0^{r_b} r^2 \rho(r) dr,$$

where  $\rho(r)$  is the electron density<sup>1</sup> at a distance  $r$  from the nucleus with charge  $Z$ . The number of valence electrons,  $N^v$ , found beyond the boundary surface defined by  $r_b$  is given by a similar integral, but spanning from  $r_b$  to infinity. The proper definition of  $N^c$  (and thus of  $N^v$ ) ultimately depends on that of  $r_b$ .  $N^c = 2$  e or  $N^c = 2$  and 10 e for the first- or second-row elements, respectively, turn out to be the only acceptable solutions.

<sup>1</sup> We write  $\rho(\mathbf{r}) = \rho(r)$  because of the assumed spherical symmetry of the electronic density; see [5]

The valence-region energy – i.e., with a change in sign, the energy required to remove the valence electrons – is

$$E^v = \frac{1}{3}(T^v + 2V^v), \quad (1)$$

where  $T^v$  and  $V^v$  are, respectively, the kinetic and potential energies of the  $N^v$  valence electrons. For the ion left behind after removal of the valence electronic charge we get

$$E^{\text{ion}} = \frac{1}{3}[T^c + 2(V_{\text{ne}}^c + V_{\text{ee}}^{\text{cc}})], \quad (2)$$

where  $T^c$  is the kinetic energy of the  $N^c$  core electrons,  $V_{\text{ne}}^c$  their nuclear-electronic potential energy and  $V_{\text{ee}}^{\text{cc}}$  their interelectronic repulsion. Equations (1) and (2) were successfully tested both at the SCF level, near the Hartree–Fock limit [1, 3], and in non-relativistic post-Hartree–Fock calculations [4], using extensive comparisons with experimental ionization potentials.

Here we wish to show that *the same real-space formulas apply to molecules* as well, but  $V^v$  must be redefined since it must now incorporate the internuclear repulsion energy,  $V_{\text{nn}}$ , and also accommodate usually more than one single core. As concerns  $E^{\text{ion}}$  and the terms appearing in Eq. (2), however, they need not be redefined. With  $E_k^{\text{ion}}$  for the energy of the  $k$ th ionic core (say,  $\text{H}^+$ ,  $\text{C}^{+4}$ ,  $\text{N}^{+5}$ ,  $\text{O}^{+6}$ ) and  $E$  for the molecule – all energies referring to ground states – the valence energy  $E^v$  under consideration satisfies the important constraint

$$E = E^v + \sum_k E_k^{\text{ion}}. \quad (3)$$

So we begin with  $E^v$ , in real space. Then, for the purpose of setting our approach in perspective, we discuss its relation to the familiar methods in orbital space. Finally, we examine the relative merits of the two models. Motivation is drawn from the fact that real-space philosophy largely governs popular atom-by-atom and bond-by-bond descriptions of molecules, while current core-valence separation schemes for molecules are rooted in orbital-space theory, with no provision for real-space applications. That should be remedied.

## 2 Theory: the core-valence separation in real space

In writing Eq. (3) we assume that all particles, the molecule and the ions, are at rest and that the molecule is at its equilibrium geometry. The total energy of the latter,  $E = \langle \Psi | \hat{H} | \Psi \rangle$ , is expressed in the Born–Oppenheimer approximation. Its derivative  $(\partial E / \partial Z_k)_\rho$  at constant electron density  $\rho$  with respect to the nuclear charge of one of its nuclei is obtained with the help of the Hellmann–Feynman theorem [6]. So we get the potential at the center  $k$ ,  $V_k / Z_k = (\partial E / \partial Z_k)_\rho$ , and the corresponding potential energy

$$\begin{aligned} V_k &= Z_k (\partial E / \partial Z_k)_\rho \\ &= -Z_k \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|} d\mathbf{r} + Z_k \sum_{l \neq k} \frac{Z_l}{R_{kl}}, \end{aligned} \quad (4)$$

where  $\rho(\mathbf{r})$  is the electron density in the volume element  $d\mathbf{r}$  at the point  $\mathbf{r}$  and  $\mathbf{R}_k$  defines the position of nucleus  $Z_k$ .  $R_{kl}$  is the distance between nuclei with charges  $Z_k$  and  $Z_l$ . Summation over all centers  $k$  gives

$$\sum_k V_k = V_{\text{ne}} + 2V_{\text{nn}}, \quad (5)$$

where  $V_{\text{nn}} = \sum_k \sum_{l > k} Z_k Z_l / R_{kl}$  is the familiar internuclear repulsion and

$$V_{\text{ne}} = - \sum_k Z_k \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|} d\mathbf{r} \quad (6)$$

measures the nuclear-electronic attraction energy.

The molecule is taken in its equilibrium geometry. So we apply the molecular virial theorem,  $2E = V_{\text{ne}} + V_{\text{ee}} + V_{\text{nn}}$ , where  $V_{\text{ee}}$  is the interelectronic repulsion. Using Eqs. (4) and (5) we get

$$2E - \sum_k Z_k \left( \frac{\partial E}{\partial Z_k} \right)_\rho = V_{\text{ee}} - V_{\text{nn}}. \quad (7)$$

On the other hand, in Hartree–Fock theory the total energy is  $E = \sum_i v_i \varepsilon_i - (V_{\text{ee}} - V_{\text{nn}})$ , where  $v_i$  is the occupation (0, 1 or 2) of orbital  $i$  with eigenvalue  $\varepsilon_i$ . Combining this result with (7) to get rid of its  $(V_{\text{ee}} - V_{\text{nn}})$  part, we write

$$(3 - \gamma)E = \sum_i v_i \varepsilon_i, \quad (8)$$

where  $\gamma$  has been defined as<sup>2</sup>

$$\gamma = \frac{1}{E} \sum_k Z_k \left( \frac{\partial E}{\partial Z_k} \right)_\rho. \quad (9)$$

Equations (4), (5) and (9) indicate that  $E = \gamma^{-1}(V_{\text{ne}} + 2V_{\text{nn}})$  for a molecule. For isolated atoms, this equation reduces to  $E = \gamma^{-1}V_{\text{ne}}$ . Finally, for an atom  $k$

embedded in a ground-state molecule, the corresponding expression is [12–16]

$$E_k = \frac{1}{\gamma_k} V_k \quad (10)$$

subject to the constraint that the average of the  $(1/\gamma_k)$  values, weighted by  $V_k$ , must restore the  $1/\gamma$  of Eq. (9). This definition of  $\gamma_k$  gives  $E = \sum_k E_k$  [3], [12]–[16], i.e., the result  $E = \gamma^{-1}(V_{\text{ne}} + 2V_{\text{nn}})$  indicated above.

The potential energy to be used in Eq. (10) is that shown in Eq. (4). Now we rewrite Eq. (4) but introduce two modifications. (1) We separate the nuclear-electronic potential energy contributed by the core electrons associated with  $Z_k$ , which is  $V_{\text{ne},k}^c$ , from that due to all the electronic charge found outside the core region of atom  $k$ . (2) We consider that the core electrons associated with  $Z_k$  do interact with the charges found outside that core. On the one hand, they repel these ‘external’ electrons and thus reduce their effective attraction by nucleus  $Z_k$ . This attraction by  $Z_k$  and the concurrent repulsion by  $N_k^c$  play similar roles, one interaction opposing the other, and are considered jointly. On the other hand, the core electrons  $N_k^c$  attract the nuclei  $Z_l \dots$  and thus counteract the repulsion between  $Z_k$  and the other nuclei. These repulsions and counteracting attractions also belong together. In short, the core electrons not only screen the attraction between  $Z_k$  and the outer electrons but also screen the internuclear repulsion involving  $Z_k$ . The total screening imputable to  $N_k^c$  is written

$V_k^{\text{cv}}$  = interaction energy between the  $N_k^c$  core electrons and the electronic and nuclear charges found outside the  $k$ th core containing  $Z_k$  and  $N_k^c$ .

The form of Eq. (4) that reflects this model is

$$\begin{aligned} V_k &= \left[ -Z_k \int_{r_{b,k}}^{\infty} \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|} d\mathbf{r} + Z_k \sum_{l \neq k} \frac{Z_l}{R_{kl}} + V_k^{\text{cv}} \right] \\ &\quad + (V_{\text{ne},k}^c - V_k^{\text{cv}}). \end{aligned} \quad (11)$$

So we go back to Eq. (10), use Eq. (11) and write  $E_k$  as

$$\begin{aligned} E_k &= \frac{1}{\gamma_k^v} \left[ -Z_k \int_{r_{b,k}}^{\infty} \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|} d\mathbf{r} + Z_k \sum_{l \neq k} \frac{Z_l}{R_{kl}} + V_k^{\text{cv}} \right] \\ &\quad + \frac{1}{\gamma_k^c} (V_{\text{ne},k}^c - V_k^{\text{cv}}), \end{aligned} \quad (12)$$

where the  $(1/\gamma_k)$  parameter of Eq. (10) is treated as the average of  $1/\gamma_k^v$  (weighted by the term in brackets) and of  $1/\gamma_k^c$  (with a weight of  $V_{\text{ne},k}^c - V_k^{\text{cv}}$ ). This description of  $E_k$  is noncommittal as to whether the  $\gamma_k$  of Eq. (10) suits the individual core and valence parts. The first part of the right-hand side of Eq. (12) represents the valence-region energy of atom  $k$  embedded in the molecule and the second term is the energy,  $E_k^{\text{ion}} = (V_{\text{ne},k}^c - V_k^{\text{cv}}) / \gamma_k^c$ , of the ionic core  $k$ . The total energy  $E = \sum_k E_k$  is thus

$$\begin{aligned} E &= \frac{1}{\gamma^v} \sum_k \left[ -Z_k \int_{r_{b,k}}^{\infty} \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|} d\mathbf{r} + Z_k \sum_{l \neq k} \frac{Z_l}{R_{kl}} + V_k^{\text{cv}} \right] \\ &\quad + \sum_k E_k^{\text{ion}}, \end{aligned} \quad (13)$$

<sup>2</sup> The interest spurred by  $\gamma$  is rooted in the fact that  $\gamma = \frac{2}{3}$  is the characteristic homogeneity of both Thomas–Fermi [7–9] and local density functional theory [10], in which case one obtains the Ruedenberg approximation,  $E = \frac{3}{2} \sum_i v_i \varepsilon_i$  [11], and Politzer’s formula  $E = \frac{3}{2} (V_{\text{ne}} + 2V_{\text{nn}})$  [12], but the actual numerical value of  $\gamma$  is of no concern in the present context

where  $1/\gamma^v$  is the appropriate average of the individual  $(1/\gamma_k^v)$  values, weighted by the terms in brackets in Eq. (13). The first right-hand side term of Eq. (13) describes the valence-region energy of a molecule,  $E^v$ . Equation (13) is a form of Eq. (3).

Up to now, potential energies were at the center of our attention. Little attention was paid to the electronic kinetic energy. This situation arose from our application of the Hellmann–Feynman theorem with intent to bring out the role of the potential energies – a role made explicit in Eq. (13) – while the kinetic energy component was seemingly neglected. In fact, it is somehow hidden in  $\gamma^v$ . We shall now calculate  $\gamma^v$  and thus reintroduce explicitly the appropriate valence electronic kinetic energy  $T^v$  into the expression describing  $E^v$ .

Let us begin with Eq. (3) and write, with Eqs. (11) to (13) in mind,

$$\gamma E = \gamma^v E^v + \gamma^c \sum_k E_k^{\text{ion}}. \quad (14)$$

[The right-hand side of Eq. (14) is, from Eqs. (12) and (13) and comparison with Eq. (5), equal to  $V_{\text{ne}} + 2V_{\text{nn}}$ , which is  $\gamma E$ .] Now use Eqs. (3) and (14) and write

$$(3 - \gamma)E = (3 - \gamma^v)E^v + (3 - \gamma^c) \sum_k E_k^{\text{ion}}. \quad (15)$$

The  $(3 - \gamma)E$  term is well known, Eq. (8). In the latter,  $v_i$  is the occupation of the orbital whose energy is  $\varepsilon_i$ . Here we use  $v_i = N_i^c + N_i^v$ , so that  $(3 - \gamma)E = \sum_i N_i^v \varepsilon_i + \sum_i N_i^c \varepsilon_i$ . Consequently, we get from Eq. (15) that

$$\left[ (3 - \gamma^v)E^v - \sum_i N_i^v \varepsilon_i \right] + \left[ (3 - \gamma^c) \sum_k E_k^{\text{ion}} - \sum_i N_i^c \varepsilon_i \right] = 0. \quad (16)$$

The latter equation achieves a separation of the core and valence contributions. The terms in brackets are certainly individually zero at the limits  $N^c = 0$  and  $N^v = 0$ . Here we postulate that physically meaningful core populations exist that allow such a core-valence separation and proceed with

$$(3 - \gamma^v)E^v = \sum_i N_i^v \varepsilon_i \quad (17)$$

for the valence region. Now we compare this expression with the  $E^v$  appearing in Eq. (13), eliminate  $\gamma^v$  and obtain

$$E^v = \frac{1}{3} \left[ \sum_k \left( -Z_k \int_{r_{b,k}}^{\infty} \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|} d\mathbf{r} + Z_k \sum_{l \neq k} \frac{Z_l}{R_{kl}} + V_k^{\text{cv}} \right) + \sum_i N_i^v \varepsilon_i \right]. \quad (18)$$

This formula can be simplified. The first term of its right-hand side is  $V_{\text{ne}}^v = V_{\text{ne}} - \sum_k V_{\text{ne},k}^c$ , i.e., the total nuclear-electronic potential energy of the molecule, Eq. (6), stripped of all the individual core nuclear-electronic interactions,  $V_{\text{ne},k}^c$ . Next, we decompose  $\sum_k V_k^{\text{cv}}$ :

$$\sum_k V_k^{\text{cv}} = V_{\text{ee}}^{\text{cv}} + 2V_{\text{ee}}^{\text{inter}} + V_{\text{ne}}^{\text{inter}}, \quad (19)$$

where  $V_{\text{ee}}^{\text{cv}}$  is the repulsion between core and valence electrons.  $V_{\text{ee}}^{\text{inter}}$  is the core-other-core interelectronic repulsion and  $V_{\text{ne}}^{\text{inter}}$  is the core-other-nucleus attraction. So we get from (18) that

$$E^v = \frac{1}{3} \left( V_{\text{ne}}^v + V_{\text{ne}}^{\text{inter}} + V_{\text{ee}}^{\text{cv}} + 2V_{\text{ee}}^{\text{inter}} + 2V_{\text{nn}} + \sum_i N_i^v \varepsilon_i \right). \quad (20)$$

$E^v$  is almost in its final form. The last step concerns  $\sum_i N_i^v \varepsilon_i$ .

Consider the Hartree–Fock equation  $\hat{F}\phi_i = \varepsilon_i \phi_i$  (in conventional notation). Multiplication from the left by  $\phi_i^*$ , integration over the space allotted to the valence electrons and summation over all occupied orbitals  $i$  leads to

$$\sum_i \int^{\text{val}} v_i \phi_i^* \hat{F} \phi_i d\tau = \sum_i \int^{\text{val}} v_i \phi_i^* \varepsilon_i \phi_i d\tau. \quad (21)$$

The integral  $N_i^v = v_i \int^{\text{val}} \phi_i^* \phi_i d\tau$  represents the number of electrons of orbital  $i$  found in the valence region. Equation (21) thus becomes

$$\sum_i \int^{\text{val}} v_i \phi_i^* \hat{F} \phi_i d\tau = \sum_i N_i^v \varepsilon_i. \quad (22)$$

The left-hand side of Eq. (22) will tell us what to use in Eq. (20) instead of  $\sum_i N_i^v \varepsilon_i$ . As concerns the one-electron terms, the integrals carried out solely over the valence space yield the nuclear-electronic potential energy,  $V_{\text{ne}}^v - V_{\text{ne}}^{\text{inter}}$ , of the  $N^v$  valence electrons plus the kinetic energy,  $T^v$ , of the same. As concerns the two-electron integrals, the left-hand side of Eq. (22) collects all the pertinent Coulomb and exchange terms between the valence electrons and those assigned to the cores – i.e.,  $V_{\text{ee}}^{\text{cv}}$  – as well as the repulsions involving exclusively valence electrons,  $V_{\text{ee}}^{\text{vv}}$ . A double-counting of the latter occurs during the summation over all  $i$ s. Eventually we get [1–3]

$$\sum_i N_i^v \varepsilon_i = T^v + V_{\text{ne}}^v - V_{\text{ne}}^{\text{inter}} + V_{\text{ee}}^{\text{cv}} + 2V_{\text{ee}}^{\text{vv}}. \quad (23)$$

Finally, we use this expression in Eq. (20) and obtain

$$E^v = \frac{1}{3} [T^v + 2(V_{\text{ne}}^v + V_{\text{ee}}^{\text{vv}} + V_{\text{ee}}^{\text{cv}} + V_{\text{ee}}^{\text{inter}} + V_{\text{nn}})]. \quad (24)$$

The sum  $V_{\text{ee}}^v = V_{\text{ee}}^{\text{vv}} + V_{\text{ee}}^{\text{cv}} + V_{\text{ee}}^{\text{inter}}$  represents the total interelectronic repulsion stripped of all core contributions, i.e.,  $V_{\text{ee}} - \sum_k V_{\text{ee},k}^{\text{cc}}$ . We also define

$$V^v = V_{\text{ne}}^v + V_{\text{ee}}^v + V_{\text{nn}}. \quad (25)$$

Equation (24) thus transforms to give Eq. (1). *The valence regions of molecules and isolated ground-state atoms or ions are described by the same formula*, Eq. (1). For isolated atoms, of course, we use  $V_{\text{ee}}^{\text{inter}} = 0$ ,  $V_{\text{ne}}^{\text{inter}} = 0$  and  $V_{\text{nn}} = 0$ .

Our formula for  $E^{\text{ion}}$ , Eq. (2), proceeds from the same general approach. Here we start off with  $E_k^{\text{ion}} = (1/\gamma_k^c)$

( $V_{\text{ne},k}^{\text{c}} - V_k^{\text{cv}}$ ), introduce  $(3 - \gamma^{\text{c}}) \sum_k E_k^{\text{ion}} = \sum_i N_i^{\text{c}} \epsilon_i$  [from Eq. (16)] and follow the pattern outlined for  $E^{\text{v}}$ . Note that  $E^{\text{v}}$  and  $E^{\text{ion}}$  add up to  $E = \frac{1}{3}(T + 2V)$ , where  $T$  and  $V$  are the total kinetic and potential energies, respectively, of a ground-state atom or molecule with energy  $E$ . Since the virial theorem applies in this situation, so that  $E = \frac{1}{2}V$ , our formula reverts back to the familiar one,  $E = T + V$ , for the entire system. Note, however, that the virial theorem does not apply to the individual core and valence subsystems.

The description presented here for the molecules is a generalization of that offered earlier [1]–[4] for the atoms and contains the latter as special case.

### 3 Interface with core-valence separations in the orbital model

In the valence molecular calculations, one can decompose the total molecular energy as follows:

$$E = E_{\text{valence}} + E_{\text{core}} + \sum_{k>l} \sum \frac{Z_k Z_l}{|\mathbf{R}_k - \mathbf{R}_l|}. \quad (26)$$

$E_{\text{core}}$  is the energy contribution from the core orbitals. If the latter are classified according to the nuclear center on which they are located (e.g., on nucleus  $k$ ), the set of core orbitals belonging to this center is  $\{\phi_c, c \in k\}$ . Moreover, if these core orbitals are assumed to be non-overlapping, then the core energy may be partitioned into two terms [17]:

$$E_{\text{core}} = E_{\text{core}}^{(1)} + E_{\text{core}}^{(2)}. \quad (27)$$

The one-center term

$$E_{\text{core}}^{(1)} = \sum_k \left[ \sum_{c \in k} 2 \langle \phi_c | -\frac{1}{2} \nabla^2 - \frac{Z_k}{|\mathbf{r} - \mathbf{R}_k|} | \phi_c \rangle + \sum_{c \in k} \sum_{c' \in k} (2J_{cc'} - K_{cc'}) \right] \quad (28)$$

is the sum of the Hartree–Fock core energies associated with each center  $k$ , so that we can identify  $E_{\text{core}}^{(1)} = \sum_k E_k^{\text{ion}}$ . The two-center term

$$E_{\text{core}}^{(2)} = 2 \sum_{k \neq l} \sum_{c \in l} \sum_{c' \in l} \langle \phi_c | -\frac{Z_k}{|\mathbf{r} - \mathbf{R}_k|} | \phi_{c'} \rangle + \sum_{k \neq l} \sum_{c \in k} \sum_{c' \in l} (2J_{cc'} - K_{cc'}) \quad (29)$$

collects the core–other–nucleus attraction terms as well as the core–other–core repulsions.  $E_{\text{core}}^{(2)}$  vanishes when the cores are infinitely separated. At this point, a comparison of Eq. (3) with Eq. (26) shows that

$$E^{\text{v}} = E_{\text{valence}} + E_{\text{core}}^{(2)} + \sum_{k>l} \sum \frac{Z_k Z_l}{|\mathbf{R}_k - \mathbf{R}_l|}. \quad (30)$$

Now we go along with an argument offered by Kahn et al. [17]. In the evaluation of Eq. (29), and consistent with the nonoverlapping core orbitals assumption, we can neglect the core–other–core exchange interactions. Because the core charge densities  $\rho_k(\mathbf{r}) = 2 \sum_{c \in k} \phi_c^*$

( $\mathbf{r}$ )  $\phi_c(\mathbf{r})$  are spherically symmetric about their nuclear centers and the cores are assumed to be nonoverlapping, one obtains the approximation [17]

$$E_{\text{core}}^{(2)} + \sum_{k>l} \sum \frac{Z_k Z_l}{|\mathbf{R}_k - \mathbf{R}_l|} \cong \sum_{k>l} \sum \frac{(Z_k - N_k^{\text{c}})(Z_l - N_l^{\text{c}})}{|\mathbf{R}_k - \mathbf{R}_l|} \quad (31)$$

and thus

$$E^{\text{v}} \cong E_{\text{valence}} + \sum_{k>l} \sum \frac{(Z_k - N_k^{\text{c}})(Z_l - N_l^{\text{c}})}{|\mathbf{R}_k - \mathbf{R}_l|}. \quad (32)$$

In this approximation, the net effect of the core interaction energy is to shield the nuclear charges in the internuclear repulsion energy.

Let us briefly state where we stand.  $E_{\text{valence}}$  is for occupied valence orbitals only and is simply represented by the straight sum of their pertinent kinetic and potential energies computed over the entire coordinate space.  $E^{\text{v}}$ , in contrast, represented by  $\frac{1}{3}(T^{\text{v}} + 2V^{\text{v}})$ , is for all occupied orbitals but integrated only over specified (core and valence) regions of real space. The relationship between the two,  $E_{\text{valence}}$  and  $E^{\text{v}}$ , is – all things considered – surprisingly simple in view of the basic differences between the two models.

The evaluation of  $E^{\text{v}}$  – e.g., with the help of Eq. (32) – presents no difficulty, but there is another, simplified and instructive form that catches our attention.

### 4 A simple approximation for $E^{\text{v}}$

In Thomas–Fermi theory, adoption of the central field model for neutral molecules at equilibrium leads to simple energy relations – well supported by accurate SCF calculations [18] – such as  $E = \frac{2}{3}(V_{\text{ne}} + 2V_{\text{nn}})$ , a formula first proposed by Politzer [12]. Evidently, nothing of the like applies to  $E_{\text{valence}}$ , but we may well inquire how things are with  $E^{\text{v}}$ .

The key is in the treatment of core–other–core and core–other–nucleus interactions. Simple approximations were presented in that matter to get Eq. (31). The same arguments are now invoked for  $V_k^{\text{cv}}$ , approximated as follows:

$$V_k^{\text{cv}} = N_k^{\text{c}} \int_{r_{\text{b},k}}^{\infty} \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|} \mathbf{d}\mathbf{r} - N_k^{\text{c}} \sum_{l \neq k} \frac{Z_l}{R_{kl}}. \quad (33)$$

The first right-hand side term of (33) describes the repulsion between  $N_k^{\text{c}}$ , located at the point  $\mathbf{R}_k$ , and all the outer electrons. The second term describes the attraction between  $N_k^{\text{c}}$  and all the nuclei other than  $Z_k$ . Eq. (13) now becomes

$$E^{\text{v}} = \frac{1}{\gamma^{\text{v}}} \sum_k \left[ -Z_k^{\text{eff}} \int_{r_{\text{b},k}}^{\infty} \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|} \mathbf{d}\mathbf{r} + Z_k^{\text{eff}} \sum_{l \neq k} \frac{Z_l}{R_{kl}} \right] \quad (34)$$

where  $Z_k - N_k^{\text{c}}$  defines the *effective* nuclear charge  $Z_k^{\text{eff}}$ . The integral appearing in (34) runs over the entire space outside the boundary  $r_{\text{b},k}$ , hence also over regions containing the core electrons of the other nuclei. Consider instead a ‘truncated’ integral  $\int^{\text{val}} \dots \mathbf{d}\mathbf{r}$  that

avoids systematically the core electrons of all atoms, including  $N_k^c$ , i.e.,

$$\int_{r_{b,k}}^{\infty} \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|} d\mathbf{r} = \int^{\text{val}} \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|} d\mathbf{r} + \sum_{l \neq k} \frac{N_l^c}{R_{kl}}$$

and rewrite (34) as follows:

$$E^v = \frac{1}{\gamma^v} \sum_k \left[ -Z_k^{\text{eff}} \int^{\text{val}} \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|} d\mathbf{r} + Z_k^{\text{eff}} \sum_{l \neq k} \frac{Z_l^{\text{eff}}}{R_{kl}} \right]. \quad (35)$$

Then note that

$$\sum_k -Z_k^{\text{eff}} \int^{\text{val}} \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_k|} d\mathbf{r} = V_{\text{ne}}^{\text{eff}} \quad (36)$$

appropriately describes the total *effective* nuclear-electronic potential energy of the molecule, i.e., the potential energy of its valence electrons – and only those – in the field of the effective nuclear charges  $Z_k^{\text{eff}}$ ,  $Z_l^{\text{eff}}$ , etc. The summation of the nuclear repulsion terms in Eq. (35) gives  $2V_{\text{nn}}^{\text{eff}}$ , where  $V_{\text{nn}}^{\text{eff}} = \sum_k \sum_{l>k} Z_k^{\text{eff}} Z_l^{\text{eff}} / R_{kl}$  is the total repulsion between  $Z_k^{\text{eff}}$ ,  $Z_l^{\text{eff}}$ , etc. The final result is thus

$$E^v = \frac{1}{\gamma^v} (V_{\text{ne}}^{\text{eff}} + 2V_{\text{nn}}^{\text{eff}}). \quad (37)$$

This expression is reminiscent of Politzer’s Thomas–Fermi formula for molecules,  $E = \frac{3}{7}(V_{\text{ne}} + 2V_{\text{nn}})$ . It describes chemical binding in the simplest possible way, in terms of *effective potentials* at the nuclei.

## 5 Numerical examples

Table 1 reports selected CI results showing that addition or withdrawal of one electron from an electroneutral atom has little effect on the energy components of its electronic cores. It thus seems a reasonable approximation to consider the neutral atom values as reference in the forthcoming calculations. Table 2 reports the pertinent GTO[5s 3p] results for use in conjunction with molecular calculations carried out with Dunning’s GTO[5s 3p|3s] basis [21]. These results were obtained from our real-space formula for  $E^{\text{ion}}$ , Eq. (2).

**Table 1.** Kinetic and potential energies of core electrons of selected atoms and ions, A, A<sup>+</sup> and A<sup>−</sup>, for use in Eq. (2), atomic units<sup>a</sup>

Atom or ion	$T^c$	$V_{\text{ee}}^{\text{cc}}$	$V_{\text{ne}}^c$	$E^{\text{ion}}$ calcd.	$E^{\text{ion}}$ exptl. <sup>b</sup>
C <sup>+</sup>	35.4638	3.8308	−70.3472	−32.523	−32.416
C	35.3696	3.8513	−70.1708	−32.423	
C <sup>−</sup>	35.2478	3.8510	−70.0409	−32.377	
N <sup>+</sup>	49.8039	4.6395	−96.8377	−44.864	−44.802
N	49.6647	4.6572	−96.6275	−44.759	
N <sup>−</sup>	49.5478	4.6568	−96.5146	−44.723	
O <sup>+</sup>	66.7252	5.4741	−127.6279	−59.194	−59.194
O	66.5554	5.4863	−127.4102	−59.098	
O <sup>−</sup>	66.4056	5.4861	−127.2674	−59.052	

<sup>a</sup> SDCI results obtained [4] with the ANO (Atomic Natural Orbital) [7s 6p 3d] basis given in [19]

<sup>b</sup> Taken as minus the appropriate sum of ionization potentials [20]

**Table 2.** Core energies of selected atoms, atomic units<sup>a</sup>

Atom	$T^c$	$V_{\text{ee}}^{\text{cc}}$	$V_{\text{ne}}^c$	$E^{\text{ion}}$	$E_{\text{core}}^{(1)}$
C	35.3844	3.9253	−70.1985	−32.3873	−32.3602
N	49.6513	4.7353	−96.6647	−44.7358	−44.7339
O	66.6077	5.5665	−127.4352	−59.0432	−59.1071

<sup>a</sup> SCF results obtained with Dunning’s GTO[5s 3p|3s] basis [21]

The  $E_{\text{core}}^{(1)}$  energies are numerical HF evaluations of Eq. (28) [23]

Numerical Hartree–Fock calculations of  $E_{\text{core}}^{(1)}$  [23], on the other hand, convincingly show that *our results in real space are the same as those of the orbital space model*, Eq. (28), and that we are thus justified to write

$$E_k^{\text{ion}} = E_{\text{core}(k)}^{(1)} \quad (38)$$

for each individual center  $k$ . Pertinent  $E_{\text{core}}^{(1)}$  values from Eq. (28) [23] are indicated in Table 2. These Hartree–Fock results are indeed close to those given by Eq. (2). Additional Hartree–Fock results are [23] −75.4797 au (F) and −444.7455 au (Cl), compared with −75.386 au and −446.153 au, respectively, from SDCI calculations of  $E^{\text{ion}}$  using Eq. (2) [4], and experimental values of −75.595 au, and −446.356 au, respectively, from the appropriate sums of ionization potentials. The identification Eq. (38) is important because it suffices to establish the link between  $E^v$  and  $E_{\text{valence}}$ , Eq. (30), deduced from Eqs. (3), (26) and (27). Moreover, if these numerical results are now taken as a validation – without explanation, of course – of our formula for  $E^{\text{ion}}$ , Eq. (2), it follows from Eq. (3) that  $E^v$  cannot but have the form given in Eq. (1), with  $E = \frac{1}{3}(T + 2V)$  for the total energy, which reverts to the standard formula  $E = T + V$  with the use of the virial theorem.

The valence-region kinetic energy,  $T^v$ , is readily obtained by subtracting all the appropriate core kinetic energies from the calculated SCF total kinetic energy. Similarly, one obtains  $V_{\text{ne}}^v$  from the total SCF nuclear-electronic potential energy from which we subtract all the pertinent core  $V_{\text{ne}}^c$  terms. Finally, we deduce  $V_{\text{ee}}^v$  from the total SCF interelectronic repulsion energy, from which we subtract the pertinent  $V_{\text{ee}}^{\text{cc}}$  terms. The internuclear repulsion,  $V_{\text{nn}}$ , of course, is that obtained by carrying out the usual optimizations of the total SCF molecular energy. The final results are displayed in Table 3. The ‘error’,  $\Delta E$ , represents the difference between our calculation using Eqs. (3) and (1) and the SCF result: it is positive whenever  $|V/T| > 2$  and negative when  $|V/T| < 2$ .

Let us now turn to Eq. (37). The nuclear and electronic potentials at the nuclei and the appropriate  $V_{\text{ne}}^c$  values give access to  $V_k^{\text{cv}}$  through its approximation expressed in Eq. (33). So, the required internuclear repulsion energies being known, we can evaluate  $V_{\text{ne}}^{\text{eff}} + 2V_{\text{nn}}^{\text{eff}}$  for use in Eq. (37). Finally, comparison with the corresponding  $E^v$  values obtained from Eq. (1) enables the evaluation of the  $\gamma^v$  parameters of Eq. (37). [The calculation of  $\sum_k V_k^{\text{cv}}$  is practical if we proceed as indicated in Eq. (13). Alternatively, one can skip this step and use Eq. (34) which is a form of Eq. (37).] Selected results are given in Table 4.

**Table 3.** Application of Eqs. (1) and (3) for selected molecules, atomic units<sup>a</sup>

Molecule	$T^v$	$V_{ne}^v$	$V_{ee}^v$	$V_{nn}$	$E^v$	$\Delta E^b$
C <sub>2</sub>	4.6357	-65.3522	32.0608	15.0712	-10.6015	-0.0140
CH <sub>4</sub>	4.8390	-49.8395	22.1775	13.5245	-7.8120	-0.0120
C <sub>2</sub> H <sub>4</sub>	7.3098	-108.0649	50.8928	33.6233	-13.2626	-0.0182
C <sub>2</sub> H <sub>6</sub>	8.4502	-127.7946	59.6461	42.2663	-14.4380	-0.0030
C <sub>3</sub> H <sub>8</sub>	12.0952	-228.8817	108.6595	82.5597	-21.0765	-0.0047
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	15.7683	-353.4116	169.3705	134.5693	-27.7250	-0.0155
<i>i</i> -C <sub>4</sub> H <sub>8</sub>	14.5551	-320.7158	154.1553	119.4861	-26.5311	-0.0059
C <sub>6</sub> H <sub>6</sub>	18.3307	-522.1176	255.1082	203.3607	-36.3221	0.0047
N <sub>2</sub>	9.3840	-107.7574	51.1787	22.8683	-19.3456	0.0654
NH <sub>3</sub>	6.4401	-58.4697	26.4138	11.7185	-11.4116	0.0280
N <sub>2</sub> H <sub>2</sub>	10.7276	-129.8056	61.2135	32.4678	-20.5070	-0.0257
N <sub>2</sub> H <sub>4</sub>	11.6968	-149.7488	70.3847	41.0728	-21.6286	0.0505
HCN	7.7719	-98.2720	46.9096	23.9108	-15.7104	0.0131
CH <sub>2</sub> N <sub>2</sub>	13.1203	-204.4055	97.6572	61.2808	-25.9382	-0.0049
NH <sub>2</sub> CN	13.3304	-202.4348	96.8968	59.7849	-26.0586	-0.0498
CH <sub>3</sub> CN	11.3545	-186.4146	89.3394	57.8880	-22.3400	0.0380
O <sub>2</sub>	16.2673	-155.1460	72.2121	27.6771	-31.4155	0.0098
H <sub>2</sub> O	9.4319	-71.5823	32.2030	9.1950	-16.9789	-0.0087
CO	10.6469	-112.1393	52.8103	22.1348	-21.2472	0.0194
CO <sub>2</sub>	19.0035	-234.4352	110.8640	58.4157	-37.1025	-0.0134
H <sub>2</sub> CO	11.8005	-132.6016	62.1461	30.9690	-22.3908	0.0145
CH <sub>3</sub> OH	13.0380	-153.8342	71.7371	40.1893	-23.5925	-0.0034
(CH <sub>3</sub> ) <sub>2</sub> O	16.6620	-261.2893	123.8250	83.8112	-30.2148	-0.0028
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	24.0549	-515.2101	247.6725	190.2076	-43.5350	-0.0361
N <sub>2</sub> O	17.3578	-226.8735	107.8693	57.8640	-34.9742	0.1106

<sup>a</sup> SCF results obtained with the GTO(9s 5p|6s) → [5s 3p|3s] basis using Dunning’s exponents [21] and optimum contraction vectors [22]

<sup>b</sup> Taken as the difference: ( $E^v + \sum_k E_k^{\text{ion}}$ ) minus  $E_{\text{SCF}}^{\text{mol}}$

**Table 4.** Calculation of  $\sum_k V_k^{\text{cv}}$  and  $V_{ne}^{\text{eff}} + 2V_{nn}^{\text{eff}}$  and application of Eq. (37) to get  $\gamma^v$ , atomic units<sup>a</sup>

Molecule	$\sum_k V_k^{\text{cv}}$	$V_{ne}^{\text{eff}} + 2V_{nn}^{\text{eff}}$	$\gamma^v$
C <sub>2</sub>	11.7366	-23.4732	2.2141
CH <sub>4</sub>	6.1128	-16.6772	2.1349
C <sub>2</sub> H <sub>6</sub>	12.1784	-31.0835	2.1529
C <sub>3</sub> H <sub>8</sub>	18.2606	-45.5017	2.1589
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	24.3511	-59.9218	2.1613
C <sub>2</sub> H <sub>4</sub>	12.1455	-28.6721	2.1623
<i>i</i> -C <sub>4</sub> H <sub>8</sub>	24.2924	-57.4512	2.1654
C <sub>2</sub> H <sub>2</sub>	12.0906	-26.2128	2.1823
C <sub>6</sub> H <sub>6</sub>	36.2814	-79.1149	2.1781
N <sub>2</sub>	17.7202	-44.3006	2.2900
NH <sub>3</sub>	9.1173	-25.9155	2.2710
N <sub>2</sub> H <sub>4</sub>	18.1233	-49.4800	2.2877
N <sub>2</sub> H <sub>2</sub>	17.9593	-46.9107	2.2875
HCN	14.9936	-35.4568	2.2569
CH <sub>2</sub> N <sub>2</sub>	23.6326	-58.2112	2.2442
NH <sub>2</sub> CN	23.9638	-58.9012	2.2603
CH <sub>3</sub> CN	20.9833	-49.6553	2.2227
O <sub>2</sub>	24.9479	-23.4732	2.3824
H <sub>2</sub> O	12.8120	-40.3821	2.3784
CO	18.4241	-49.4456	2.3272
CO <sub>2</sub>	30.7941	-86.8096	2.3397
H <sub>2</sub> CO	18.6000	-52.0636	2.3252
CH <sub>3</sub> OH	18.7830	-54.6725	2.3174
H <sub>2</sub> CCO	24.4384	-63.6231	2.2834
(CH <sub>3</sub> ) <sub>2</sub> O	24.7477	-68.9192	2.2810
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	36.9388	-97.8560	2.2478
N <sub>2</sub> O	29.9487	-81.1968	2.3216

<sup>a</sup> SCF results using the (9s 5p|6s) → [5s 3p|3s] basis [21, 22]

The  $1/\gamma^v$  parameters introduced with Eq. (13) represent averages of individual ‘atomic’  $1/\gamma_k^v$  parameters weighted by *effective* electronic and nuclear potential energies, i.e., the terms in brackets shown in Eq. (34) or

(35) – a situation similar to that prevailing in all-electron applications of  $E = (1/\gamma)(V_{ne} + 2V_{nn})$ . In the latter case,  $1/\gamma$  ( $\approx 3/7$ ) is the average of ‘atomic’  $1/\gamma_k$  terms weighted by the *total* potential energies  $V_k$ , Eq. (4), with  $1/\gamma_k = 0.500$  (H), 0.429 (C), 0.426 (N) and 0.422 (O) [15]. Here, in our valence-region applications, we find ‘atomic’  $1/\gamma_k^v$  terms of 0.500 (H), 0.455 (C), 0.436 (N) and 0.421 (O). On the basis of the present [5s 3p|3s] SCF results alone, it is difficult to judge conclusively how accurate our approximations are, namely that proposed for  $V_k^{\text{cv}}$ , Eq. (33), but back-calculations using these  $1/\gamma_k^v$  parameters and the appropriate SCF potential energies shown in Eq. (34) reproduce the results given by Eq. (1) typically within  $\pm 0.15\%$  or better, which seems acceptable. Future, more accurate post-Hartree–Fock evaluations should reveal the full bearing of the Kahn–Baybutt–Truhlar point-charge-potential simplifications [17] introduced in Eq. (33) and thus in Eqs. (34) and (37). The  $\gamma^v$  values of Table 4 show that while hydrogen tends to lower them because of the non-negligible contribution of  $1/\gamma_k^v = 0.500$ , the observed values are generally of the order anticipated from Thomas–Fermi theory. This situation parallels that encountered in all-electron calculations of  $\gamma$  [15].

## 6 Conclusions

The partitioning of the electronic charge of a molecule into core and valence parts unfolds as a straightforward extension of the methods applied to atoms. In *real space* the valence-region energy,  $E^v$ , satisfies the constraint  $E = E^v + \sum_k E_k^{\text{ion}}$ ,  $E$  being the total ground-state energy of the molecule (or atom) under scrutiny and  $E_k^{\text{ion}}$  that of an ion  $k$  (such as H<sup>+</sup>, C<sup>4+</sup>, N<sup>5+</sup>, etc.) left behind upon removal of the entire valence-region electronic charge.

$E^v$  thus includes whatever energy changes occur when the ‘valence electrons’ are added to the ions  $k$  forced into adopting the equilibrium geometry of an incipient ground-state molecule. So it justifies, albeit in an unconventional way, its designation ‘valence energy’.

For ion  $k$  it is shown that  $E_k^{\text{ion}} = \frac{1}{3}[T^c + 2(V_{\text{ne}}^c + V_{\text{ee}}^{\text{cc}})]$ , where  $T^c$  is the kinetic energy of its  $N^c$  core electrons,  $V_{\text{ne}}^c$  their nuclear-electronic potential energy and  $V_{\text{ee}}^{\text{cc}}$  their interelectronic repulsion. In SCF theory, on the other hand,  $E^{\text{ion}}$  is identified with the appropriate sum of its Hartree–Fock core energies. As a direct consequence, the familiar orbital-space valence energy,  $E_{\text{valence}}$ , and our real-space  $E^v$  energy are related to one another in a straightforward manner, e.g., by the approximation  $E^v = E_{\text{valence}} + V_{\text{nn}}^{\text{eff}}$  that highlights the role of the repulsions between nuclei partially screened by their core electrons.  $E_{\text{valence}}$  is the usual straight sum of the pertinent kinetic and potential energies of the occupied valence orbitals computed over the entire coordinate space, whereas  $E^v$  is for all occupied orbitals, but integrated only over specified (core and valence) regions of real space. The relationship between  $E^v$  and  $E_{\text{valence}}$  offers nothing beyond what seems most obvious on simple physical grounds: the novelty is in the form,  $E^v = \frac{1}{3}(T^v + 2V^v)$ , of the valence energy in our real-space partitioning, where  $T^v$  and  $V^v$  are, respectively, the relevant valence kinetic and potential energies.

Our description surely means that  $E^v$  accounts for chemical binding, which makes it particularly attractive in real-space applications to molecules. Indeed, any atom-by-atom or bond-by-bond partitioning of a molecule – such as Bader’s atom-in-the-molecule model [24] – is by its very nature treated in real space. In this particular context, we surely benefit from the fact that our real-space core-valence partitioning correctly reflects chemical binding. Its formulation with intent to define bond energies [3,14] or the energies of ‘atoms-in-the-molecule’ [24], however, meets with the usual difficulties that are encountered when it comes down to fairly distributing interelectronic and internuclear repulsion terms among chemical bonds or ‘atoms in the molecule’: these terms are not simply separable into atomic or bond contributions. And yet, with the help of our Thomas–Fermi-like approximation  $E^v = (1/\gamma^v)(V_{\text{ne}}^{\text{eff}} + 2V_{\text{nn}}^{\text{eff}})$ , we get round this sort of problem, as  $E^v$  is then expressed solely in terms of the appropriate effective potentials at the individual nuclei, which raise no partitioning-related problems. The new problem – namely that brought up by  $1/\gamma^v$  – can be solved (in principle) remembering that this parameter is a weighted average of atomic  $1/\gamma_k^v$

terms which can be treated, at least to a good approximation, as constants for each type of atom  $k$ .

In short, our core-valence partitioning in real space offers the advantage of being naturally best suited in problems concerned with real-space atom-by-atom decompositions of molecules. Yet, though serving different purposes, and however different they may seem, real-space and orbital-space core-valence separations appear for what they are: two facets of the same reality.

*Acknowledgements.* We thank Professor Vincenzo Barone, Dr. Mark E. Casida and Mr. Pierre-Nicholas Roy for most helpful discussions and the FCAR, Québec, for financial support.

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