Theor Chem Acc (2004) 111:395–399
DOI 10.1007/s00214-003-0533-4

Theoretical
Chemistry Accounts

Regular article

Atomic and molecular energies as functionals of the electrostatic potential

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Received: 10 January 2003 / Accepted: 30 April 2003 / Published online: 3 February 2004

Abstract. Starting from the Hohenberg–Kohn theorem, atomic and molecular energies have been expressed rigorously as functionals of the electronic electrostatic potential, $V_{\mathrm{elec}}(\mathbf{r})$. Explicit formulations have been derived for the functionals representing the kinetic energy and electronic interaction contributions to the total energies.

Keywords: Electrostatic potentials – Energies – Electronic density

Introduction

It was the work of Scrocco, Tomasi and their colleagues that led to the emergence and eventual wide adoption of the molecular electrostatic potential as a tool for interpreting and predicting molecular interactive behavior. The first paper appeared in 1970 [1] and was followed by many more, with reviews being published in 1973 [2] and 1978 [3]. (For an excellent account of the origins and evolution of this program, see Tomasi et al. [4].) Prior to this, theoretical analyses of molecular reactivity had largely focused upon various proposed indices, such as atomic charges, free valencies, frontier electron densities, localization energies, etc. [5, 6, 7, 8, 9, 10, 11, 12, 13]. While these can sometimes produce useful insights and correlations, they are defined quantities, and therefore inherently arbitrary. In contrast, the electrostatic potential is a real physical property, an observable, which can be determined experimentally, by diffraction techniques [14, 15, 16, 17, 18] as well as computationally. Thus it provides a more rigorous basis for analyzing reactive behavior, and has indeed been used quite successfully for this purpose, particularly for noncovalent interactions and the early stages of processes that involve bond rupture/formation and/or charge polarization [1, 2, 3, 4, 14, 19, 20, 21, 22, 23, 24, 25, 26].

The electrostatic potential $V(\mathbf{r})$ at any point $\mathbf{r}$ in the space of a system of nuclei and electrons is the sum of nuclear and electronic contributions,

$$V(\mathbf{r}) = V_{\mathrm{nuc}}(\mathbf{r}) + V_{\mathrm{elec}}(\mathbf{r}) \tag{1}$$

where

$$V_{\mathrm{nuc}}(\mathbf{r}) = \sum_{\mathrm{A}} \frac{Z_{\mathrm{A}}}{|\mathbf{R}_{\mathrm{A}} - \mathbf{r}|} \tag{2}$$

and

$$V_{\mathrm{elec}}(\mathbf{r}) = -\int \frac{\rho(\mathbf{r}')\mathrm{d}\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \tag{3}$$

Z_{A} is the charge on nucleus A, located at $\mathbf{R}_{\mathrm{A}}$, and $\rho(\mathbf{r})$ is the electronic density. The latter is intimately linked to $V_{\mathrm{elec}}(\mathbf{r})$ and $V(\mathbf{r})$, not only through Eqs. 1 and 3 but also via Poisson's equation, in either the form

$$\nabla^2 V_{\mathrm{elec}}(\mathbf{r}) = 4\pi\rho(\mathbf{r}) \tag{4}$$

or

$$\nabla^2 V(\mathbf{r}) = 4\pi\rho(\mathbf{r}) - 4\pi\sum_{\mathrm{A}} Z_{\mathrm{A}}\delta(\mathbf{R}_{\mathrm{A}} - \mathbf{r}) \tag{5}$$

In 1964, Hohenberg and Kohn showed that $\rho(\mathbf{r})$ determines the nuclear potential $V_{\mathrm{nuc}}(\mathbf{r})$ of a ground-state system and therefore specifies its Hamiltonian [27]; thus the electronic energy is a functional of the electronic density:

Contribution to the Jacopo Tomasi Honorary Issue

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$$E_{\mathrm{elec}} = E_{\mathrm{elec}}[\rho(\mathbf{r})] \tag{6}$$

Since the contribution of the nuclear–electronic interaction to the electronic energy is known exactly,

$$V_{\mathrm{ne}} = -\sum_{\mathrm{A}} \int \frac{Z_{\mathrm{A}}}{|\mathbf{R}_{\mathrm{A}} - \mathbf{r}|} \rho(\mathbf{r}) \mathrm{d}\mathbf{r} \tag{7}$$

then E_{elec} $[\rho(\mathbf{r})]$ can be expressed rigorously as [27]

$$E_{\mathrm{elec}}[\rho(\mathbf{r})] = -\sum_{\mathrm{A}} \int \frac{Z_{\mathrm{A}}}{|\mathbf{R}_{\mathrm{A}} - \mathbf{r}|} \rho(\mathbf{r}) \mathrm{d}\mathbf{r} + F[\rho(\mathbf{r})] \tag{8}$$

The functional $F[\rho(\mathbf{r})]$ represents the kinetic and the interelectronic repulsion energies,

$$F[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] + V_{\mathrm{ee}}[\rho(\mathbf{r})] \tag{9}$$

and is not known, although considerable progress has been made in developing effective formulations of it [28, 29, 30, 31, 32]; these have led to the evolution of density functional theory into a powerful computational tool.

The electrostatic potential produced by the electrons at any nucleus A is given by

$$V_{0,\mathrm{A,elec}} = -\int \frac{\rho(\mathbf{r})}{|\mathbf{R}_{\mathrm{A}} - \mathbf{r}|} \mathrm{d}\mathbf{r} \tag{10}$$

Combining Eq. 10 with the electronic energy functional, Eq. 8, and invoking Eq. 4 yields

$$E_{\mathrm{elec}}[V_{\mathrm{elec}}(\mathbf{r})] = \sum_{\mathrm{A}} Z_{\mathrm{A}} V_{0,\mathrm{A,elec}} + \Im[V_{\mathrm{elec}}(\mathbf{r})] \tag{11}$$

where $\Im[V_{\mathrm{elec}}(\mathbf{r})]$ is the functional analogue of $F[\rho(\mathbf{r})]$. The total energy is obtained by adding the internuclear interaction term

$$V_{\mathrm{nn}} = \frac{1}{2} \sum_{\mathrm{A}} Z_{\mathrm{A}} \sum_{\mathrm{B} \neq \mathrm{A}} \frac{Z_{\mathrm{B}}}{|\mathbf{R}_{\mathrm{B}} - \mathbf{R}_{\mathrm{A}}|} = \frac{1}{2} \sum_{\mathrm{A}} Z_{\mathrm{A}} V_{0,\mathrm{A,nuc}} \tag{12}$$

in which Eq. 2 was used to replace the second summation. Thus,

$$E_{\mathrm{tot}}[V_{\mathrm{elec}}(\mathbf{r})] = E_{\mathrm{elec}}[V_{\mathrm{elec}}(\mathbf{r})] + V_{\mathrm{nn}} \tag{13}$$

$$= \sum_{\mathrm{A}} Z_{\mathrm{A}} V_{0,\mathrm{A,elec}} + \Im[V_{\mathrm{elec}}(\mathbf{r})] + \frac{1}{2} \sum_{\mathrm{A}} Z_{\mathrm{A}} V_{0,\mathrm{A,nuc}} \tag{14}$$

$$= \sum_{\mathrm{A}} Z_{\mathrm{A}} \left[V_{0,\mathrm{A,elec}} + \frac{1}{2} V_{0,\mathrm{A,nuc}} \right] + \Im[V_{\mathrm{elec}}(\mathbf{r})] \tag{15}$$

Equations 11 and 15 show that both E_{elec} and E_{tot} can be viewed, rigorously, as functionals of $V_{\mathrm{elec}}(\mathbf{r})$. This statement is not contradicted by the presence of $V_{0,\mathrm{A,nuc}}$ in Eq. 15 because $V_{\mathrm{nuc}}(\mathbf{r})$ is determined by $\rho(\mathbf{r})$ (Hohenberg–Kohn theorem) which in turn is related to $V_{\mathrm{elec}}(\mathbf{r})$ by Poisson's equation. Thus, as has been pointed out on several occasions recently [33, 34, 35, 36, 37], the role of the electrostatic potential is a very fundamental one, not limited to analyzing molecular reactivity. Equations 11 and 15 indicate the possibility of relating it *exactly* to atomic and molecular energies. This has been done, by means of the Hellmann–Feynman theorem, as shall now be discussed. We shall also develop explicit representations of the functional $\Im[V_{\mathrm{elec}}(\mathbf{r})]$.

Exact atomic and molecular energy formulas

Atoms

For a system having energy E, Hamiltonian H, and described by the wave function Ψ such that $E = \langle \Psi | \mathrm{H} | \Psi \rangle$, the Hellmann–Feynman theorem states that [38, 39]

$$\frac{\partial E}{\partial \lambda} = \left\langle \Psi \left| \frac{\partial \mathrm{H}}{\partial \lambda} \right| \Psi \right\rangle \tag{16}$$

in which λ is any parameter appearing in H and the derivatives are taken with all other parameters being held constant.

For an N-electron atom with energy E^{at}, it follows that [40, 41, 42, 43]

$$\left(\frac{\partial E^{\mathrm{at}}}{\partial Z} \right)_N = -\int \frac{\rho(\mathbf{r}) \mathrm{d}\mathbf{r}}{\mathbf{r}} = V_{0,\mathrm{elec}} \tag{17}$$

where $V_{0,\mathrm{elec}}$ is the electrostatic potential at the nucleus due to the electrons, Eq. 10, with $\mathbf{r}$ being measured from the nucleus. Integration of Eq. 17 yields [40, 44, 45]

$$E^{\mathrm{at}} = \int_{Z'=0}^{Z} \left[V_{0,\mathrm{elec}}(Z') \right]_N \mathrm{d}Z' \tag{18}$$

which can be converted by integration by parts into [44]

$$E^{\mathrm{at}} = 0.5 Z V_{0,\mathrm{elec}} - 0.5 \int_{Z'=0}^{Z} \left[Z' \left(\frac{\partial V_{0,\mathrm{elec}}(Z')}{\partial Z'} \right) - V_{0,\mathrm{elec}}(Z') \right]_N \mathrm{d}Z' \tag{19}$$

or [45]

$$E^{\mathrm{at}} = Z V_{0,\mathrm{elec}} - \int_{Z'=0}^{Z} \left[Z' \left(\frac{\partial V_{0,\mathrm{elec}}(Z')}{\partial Z'} \right) \right]_N \mathrm{d}Z' \tag{20}$$

Equations 18–20 are equivalent exact expressions that relate the energy of the atom to the electrostatic potential at its nucleus. While Eq. 18 should be the easiest to apply, the others have certain features that are of considerable conceptual interest. First, by taking the virial theorem

$$E^{\mathrm{at}} = 0.5(V_{\mathrm{ne}} + V_{\mathrm{ee}}) = 0.5ZV_{0,\mathrm{elec}} + 0.5V_{\mathrm{ee}} \tag{21}$$

in conjunction with Eq. 19, one obtains,

$$V_{\mathrm{ee}} = -\int\limits_{Z'=0}^{Z} \left[Z'\left(\frac{\partial V_{0,\mathrm{elec}}(Z')}{\partial Z'}\right) - V_{0,\mathrm{elec}}(Z')\right]_N \mathrm{d}Z' \tag{22}$$

Equation 22, rigorously formulates the two-electron property V_{ee} in terms of the one-electron $V_{0,\mathrm{elec}}$.

A more interesting result, from the standpoint of our present objectives, comes from writing the atomic version of Eq. 15,

$$E^{\mathrm{at}} = ZV_{0,\mathrm{elec}} + \Im^{\mathrm{at}}[V_{\mathrm{elec}}(\mathbf{r})] \tag{23}$$

Comparison of Eqs. 20 and 23 leads to,

$$\Im^{\mathrm{at}}[V_{\mathrm{elec}}(\mathbf{r})] = -\int\limits_{Z'=0}^{Z} \left[Z'\left(\frac{\partial V_{0,\mathrm{elec}}(Z')}{\partial Z'}\right)\right]_N \mathrm{d}Z' \tag{24}$$

The right side of Eq. 24 can be put explicitly in terms of $V_{\mathrm{elec}}(\mathbf{r})$ by invoking spherical symmetry for the atom [46] and Eq. 4; thus,

$$V_{0,\mathrm{elec}} = -\int \frac{\rho(\mathbf{r})\mathrm{d}\mathbf{r}}{\mathbf{r}} = -4\pi \int\limits_{r=0}^{\infty} r\rho(r)\mathrm{d}r \tag{25}$$

$$= -\int\limits_{r=0}^{\infty} \frac{1}{r}\frac{\partial}{\partial r}\left(r^2 \frac{\partial V_{\mathrm{elec}}(r)}{\partial r}\right)\mathrm{d}r = -\int\limits_{r=0}^{\infty} \frac{\partial^2}{\partial r^2}(rV_{\mathrm{elec}}(r))\mathrm{d}r \tag{26}$$

so that,

$$\Im^{\mathrm{at}}[V_{\mathrm{elec}}(\mathbf{r})] = \int\limits_{Z'=0}^{Z} \left[Z'\frac{\partial}{\partial Z'}\int\limits_{r=0}^{\infty} \frac{\partial^2}{\partial r^2}(rV_{\mathrm{elec}}(r,Z'))\mathrm{d}r\right]_N \mathrm{d}Z' \tag{27}$$

Molecules

For molecules, one could apply the Hellmann–Feynman theorem to obtain the analogue of Eq. 17:

$$\left(\frac{\partial E^{\mathrm{mol}}}{\partial Z_{\mathrm{A}}}\right)_{N,Z_{\mathrm{B}\neq\mathrm{A}},\{\mathbf{R}_i\}} = V_{0,\mathrm{A}} \tag{28}$$

$V_{0,\mathrm{A}}$ is the electrostatic potential at nucleus A that is produced by the electrons and other nuclei,

$$V_{0,\mathrm{A}} = \sum_{\mathrm{B}\neq\mathrm{A}} \frac{Z_{\mathrm{B}}}{|\mathbf{R}_{\mathrm{B}} - \mathbf{R}_{\mathrm{A}}|} - \int \frac{\rho(\mathbf{r})\mathrm{d}\mathbf{r}}{|\mathbf{r} - \mathbf{R}_{\mathrm{A}}|} \tag{29}$$

$$= \sum_{\mathrm{B}\neq\mathrm{A}} \frac{Z_{\mathrm{B}}}{|\mathbf{R}_{\mathrm{B}} - \mathbf{R}_{\mathrm{A}}|} + V_{0,\mathrm{A,elec}} \tag{30}$$

and the derivative in Eq. 28 is to be taken while holding fixed the number of electrons, all other nuclear charges, and all nuclear positions.

An alternative procedure, which will be adopted here, is to follow Wilson [47] and introduce into the molecular Hamiltonian a scaling parameter λ such that the charge on any nucleus is $Z'_i = \lambda z_i$, where λ can vary between zero and one. In the actual molecule, $\lambda = 1$ and $Z'_i = z_i = Z_i$. The use of λ allows all of the nuclear charges to vary in a concerted manner between zero and their true values.

Then by the Hellmann–Feynman theorem, Eq. 16, one obtains [47],

$$\left(\frac{\partial E^{\mathrm{mol}}}{\partial \lambda}\right)_{N,\{z_i\},\{\mathbf{R}_i\}}$$

$$= 2\lambda \sum_{\mathrm{A}}\sum_{\mathrm{B}>\mathrm{A}} \frac{z_{\mathrm{A}} z_{\mathrm{B}}}{|\mathbf{R}_{\mathrm{B}} - \mathbf{R}_{\mathrm{A}}|} - \sum_{\mathrm{A}} z_{\mathrm{A}} \int \frac{\rho(\mathbf{r},\lambda)\mathrm{d}\mathbf{r}}{|\mathbf{r} - \mathbf{R}_{\mathrm{A}}|} \tag{31}$$

Integrating Eq. 31 between $\lambda = 0$ and $\lambda = 1$ [47],

$$E^{\mathrm{mol}} = \sum_{\mathrm{A}}\sum_{\mathrm{B}>\mathrm{A}} \frac{Z_{\mathrm{A}} Z_{\mathrm{B}}}{|\mathbf{R}_{\mathrm{B}} - \mathbf{R}_{\mathrm{A}}|} - \sum_{\mathrm{A}} z_{\mathrm{A}} \int\limits_{\lambda=0}^{1} \int \frac{\rho(\mathbf{r},\lambda)\mathrm{d}\mathbf{r}}{|\mathbf{R}_{\mathrm{A}} - \mathbf{r}|}\mathrm{d}\lambda \tag{32}$$

It has been shown [44] that Eq. 32 can be converted to,

$$E^{\mathrm{mol}} = \sum_{\mathrm{A}} z_{\mathrm{A}} \int\limits_{\lambda=0}^{1} \left[V_{0,\mathrm{A}}(\lambda)\right]_N \mathrm{d}\lambda \tag{33}$$

(N,$\{z_i\}$ and $\{\mathbf{R}_i\}$ are to be kept constant throughout this derivation, even if this is not explicitly indicated.) Integrating Eq. 33 by parts,

$$E^{\mathrm{mol}} = \sum_{\mathrm{A}} Z_{\mathrm{A}} V_{0,\mathrm{A}} - \sum_{\mathrm{A}} z_{\mathrm{A}} \int\limits_{\lambda=0}^{1} \lambda\left[\frac{\partial V_{0,\mathrm{A}}(\lambda)}{\partial \lambda}\right]_N \mathrm{d}\lambda \tag{34}$$

Equations 33 and 34 are the molecular analogues of Eqs. 18 and 20; it is notable they correspond essentially to simply summing their atomic counterparts over the individual atoms. The molecular version of Eq. 19 has also been derived [44, 45].

Substituting for $V_{0,\mathrm{A}}$ in Eq. 34 by means of Eq. 30,

$$\begin{aligned} E^{\mathrm{mol}} &= \sum_{\mathrm{A}} Z_{\mathrm{A}} \left[V_{0,\mathrm{A,elec}} + \sum_{\mathrm{B}\neq\mathrm{A}} \frac{Z_{\mathrm{B}}}{|\mathbf{R}_{\mathrm{B}}-\mathbf{R}_{\mathrm{A}}|} \right] \\ &\quad - \sum_{\mathrm{A}} z_{\mathrm{A}} \int_{\lambda=0}^{1} \lambda \frac{\partial}{\partial\lambda} \left[V_{0,\mathrm{A.elec}}(\lambda) + \sum_{\mathrm{B}\neq\mathrm{A}} \frac{\lambda z_{\mathrm{B}}}{|\mathbf{R}_{\mathrm{B}}-\mathbf{R}_{\mathrm{A}}|} \right]_N \mathrm{d}\lambda \end{aligned} \tag{35}$$

and carrying out the integration over the nuclear term,

$$\begin{aligned} E^{\mathrm{mol}} &= \sum_{\mathrm{A}} Z_{\mathrm{A}} \left[V_{0,\mathrm{A,elec}} + \sum_{\mathrm{B}\neq\mathrm{A}} \frac{Z_{\mathrm{B}}}{|\mathbf{R}_{\mathrm{B}}-\mathbf{R}_{\mathrm{A}}|} \right] - \frac{1}{2} \sum_{\mathrm{A}} Z_{\mathrm{A}} \sum_{\mathrm{B}\neq\mathrm{A}} \frac{Z_{\mathrm{B}}}{|\mathbf{R}_{\mathrm{B}}-\mathbf{R}_{\mathrm{A}}|} \\ &\quad - \sum_{\mathrm{A}} z_{\mathrm{A}} \int_{\lambda=0}^{1} \lambda \frac{\partial}{\partial\lambda} \left[V_{0,\mathrm{A.elec}}(\lambda) \right]_N \mathrm{d}\lambda \end{aligned} \tag{36}$$

$$\begin{aligned} &= \sum_{\mathrm{A}} Z_{\mathrm{A}} V_{0,\mathrm{A,elec}} + \frac{1}{2} \sum_{\mathrm{A}} Z_{\mathrm{A}} \sum_{\mathrm{B}\neq\mathrm{A}} \frac{Z_{\mathrm{B}}}{|\mathbf{R}_{\mathrm{B}}-\mathbf{R}_{\mathrm{A}}|} \\ &\quad - \sum_{\mathrm{A}} z_{\mathrm{A}} \int_{\lambda=0}^{1} \lambda \frac{\partial}{\partial\lambda} \left[V_{0,\mathrm{A.elec}}(\lambda) \right]_N \mathrm{d}\lambda \end{aligned} \tag{37}$$

Since, by Eq. 12,

$$V_{0,\mathrm{A,nuc}} = \sum_{\mathrm{B}\neq\mathrm{A}} \frac{Z_{\mathrm{B}}}{|\mathbf{R}_{\mathrm{B}} - \mathbf{R}_{\mathrm{A}}|} \tag{38}$$

then combining Eqs. 15 and 37 gives,

$$\Im^{\mathrm{mol}}[V_{\mathrm{elec}}(\mathbf{r})] = -\sum_{\mathrm{A}} z_{\mathrm{A}} \int_{\lambda=0}^{1} \lambda \frac{\partial}{\partial\lambda} \left[V_{0,\mathrm{A.elec}}(\lambda) \right]_N \mathrm{d}\lambda \tag{39}$$

Equation 39 is the molecular version of Eq. 24.

Discussion and summary

Equations 24 and 39 are rigorous formulations of the kinetic energy and electronic interaction contributions to the total energy. Thus they are analogues of the Hohenberg–Kohn $F[\rho(\mathbf{r})]$, but written as functionals of $V_{\mathrm{elec}}(\mathbf{r})$. Again, the molecular expression is essentially a summation of its atomic counterpart over the individual atoms. As stipulated by Eq. 15, there is no nuclear interaction term in the molecular formula, Eq. 39, even though it appears in both parts of Eq. 35, from which Eq. 39 was derived.

The determination of atomic and molecular energies by means of Eqs. 18–20, 33, and 34, which are exact, encounters the problem that the integrals are to be evaluated with the number of electrons being held constant. This requirement can be avoided, however, by assuming that the chemical potentials of the systems are zero or negligible [48, 49, 50]; the integrations can then be carried out over, for example, neutral rather than isoelectronic sequences. This approach has been tested, with overall encouraging results [44, 48, 49, 50]. It could be applied as well to the evaluation of $\Im^{\mathrm{at}}[V_{\mathrm{elec}}(\mathbf{r})]$ and $\Im^{\mathrm{mol}}[V_{\mathrm{elec}}(\mathbf{r})]$ via Eqs. 24, 27, and 39, in which the restriction that N be held constant also applies. Another promising technique that we are currently investigating [51] is based upon recognition of the fact that atomic and molecular ions with charges more negative than -1 are usually not stable in the gas phase [52, 53, 54].

Our focus in this paper has been primarily upon expressing atomic and molecular energies as functionals of $V_{\mathrm{elec}}(\mathbf{r})$, taking the Hohenberg–Kohn theorem as our starting point. Other aspects of the fundamental nature of the electrostatic potential as a determinant of atomic and molecular properties have been discussed and summarized elsewhere [29, 33, 34, 36, 37 ,55, 56, 57]. They include its relationship to the chemical potential/electronegativity [33, 34, 55, 58, 59] and to covalent [37, 59, 60] and anionic [61, 62] radii. The role of the electrostatic potential with respect to molecular interactive behavior has already been mentioned. In this context, we also note the intriguing indications of a relationship between $V_{\mathrm{elec}}(\mathbf{r})$ and local hardness/polarizability [63, 64, 65, 66]. This is being studied [67].

Acknowledgements. The assistance of Dr. Jane S. Murray is greatly appreciated.

References

1. Bonaccorsi R, Scrocco E, Tomasi J (1970) J Chem Phys 52:5270
2. Scrocco E, Tomasi J (1973) Topics Curr Chem 42:95
3. Scrocco E, Tomasi J (1978) Adv Quantum Chem 11:115
4. Tomasi J, Mennucci B, Cammi R (1996) In: Murray JS, Sen K (eds) Molecular electrostatic potentials: concepts and applications. Elsevier, Amsterdam, chap 1
5. Sung SS, Chalvet O, Daudel R (1960) J Chim Phys 57:31
6. Koutecky J, Zahradnik R, Cizek J (1961) Trans Faraday Soc 57:169
7. Brown RD (1964) In: Lowdin P-O, Pullman B (eds) Molecular orbitals in chemistry, physics and biology. Academic, New York, p 485
8. Fukui K (1964) In: Lowdin P-O, Pullman B (eds) Molecular orbitals in chemistry, physics and biology. Academic, New York, p 513
9. Fukui K (1965) In: Sinanoglu O (ed) Modern quantum chemistry, part I. Academic, New York, p 49
10. Greenwood HH, McWeeny R (1966) Adv Phys Org Chem 4:73
11. Klopman G (1968) J Am Chem Soc 90:223
12. Fukui K (1971) Acc Chem Res 4:57
13. Julg A (1975) Top Curr Chem 58:1
14. Politzer P, Truhlar DG (eds) (1981) Chemical applications of atomic and molecular electrostatic potentials. Plenum, New York
15. Lecomte C, Ghermani N, Pichon-Pesme V, Souhasson M (1992) J Mol Struct (Theochem) 255:241
16. Su Z, Coppens P (1993) Z Naturforsch A: Phys Sci 48:85
17. Stewart RF, Craven BM (1993) Biophys J 65:998
18. Feil D (1996) In: Murray JS, Sen K (eds) Molecular electrostatic potentials: concepts and applications. Elsevier, Amsterdam, chap 13

19. Politzer P, Daiker KC (1981) In: Deb BM (ed) The force concept in chemistry. Van Nostrand Reinhold, New York, chap 6
20. Politzer P, Laurence PR, Jayasuriya K (1985) Env Health Persp 61:191
21. Politzer P, Murray JS (1991) In: Lipkowitz KB, Boyd DB (eds) Computational chemistry, vol 2. VCH, New York, chap 7
22. Naray-Szabo G, Ferenczy GG (1995) Chem Rev 95:829
23. Murray JS, Politzer P (1998) In: Sapse A-M (ed) Molecular orbital calculations for biological systems. Oxford University Press, New York, chap 3
24. Murray JS, Politzer P (1998) J Mol Struct (Theochem) 425:107
25. Politzer P, Murray JS (1999) Trends Chem Phys 7:157
26. Politzer P, Murray JS, Peralta-Inga Z (2001) Int J Quantum Chem 85:676
27. Hohenberg P, Kohn W (1964) Phys Rev B 136:864
28. Parr RG, Yang W (1989) Density-functional theory of atoms and molecules. Oxford University Press, New York
29. Kryachko ES, Ludena EV (1990) Energy density functional theory of many-electron systems. Kluwer, Dordrecht
30. Seminario JM, Politzer P (eds) (1995) Modern density functional theory: a tool for chemistry. Elsevier, Amsterdam
31. Parr RG, Yang W (1995) Annu Rev Phys Chem 46:701
32. Seminario JM (ed) (1996) Recent developments and applications of modern density functional theory. Elsevier, Amsterdam
33. Politzer P, Murray JS (1996) In: Murray JS, Sen K (eds) Molecular electrostatic potentials: concepts and applications. Elsevier, Amsterdam, chap 16
34. Politzer P, Murray JS (2002) Theor Chem Acc 108:134
35. Sen KD, De Proft F, Geerlings P (2002) J Chem Phys 117:4684
36. Politzer P, Lane P, Murray JS (2002) In: Sen KD (ed) Reviews in modern quantum chemistry: a celebration of the contributions of Robert G. Parr, vol I. World Scientific, Singapore, chap 4
37. Politzer P, Murray JS, Lane P (2003) J Comp Chem 24:505
38. Hellmann H (1937) Einfuhrung in die quantenchemie. Deuticke, Leipzig
39. Feynman RP (1939) Phys Rev 56:340
40. Foldy LL (1951) Phys Rev 83:397
41. Lowdin P-O (1959) J Mol Spectrosc 3:46
42. Fraga S (1964) Theor Chim Acta 2:406
43. Gaspar R (1967) Int J Quantum Chem 1:139
44. Politzer P, Parr RG (1974) J Chem Phys 61:4258
45. Politzer P (2003) In: Brandas EJ, Kryachko ES (eds) Fundamental world of quantum chemistry: a tribute to the memory of Per-Olov Lowdin. Kluwer, Dordrecht, p.631
46. Delgado-Barrio G, Prat RF (1975) Phys Rev A 12:2288
47. Wilson Jr EB (1962) J Chem Phys 36:2232
48. Politzer P (1984) J Chem Phys 80:380
49. Politzer P, Jin P, Jalbout AF, Murray JS (2002) Acta Phys Chim Debr 34–35:349
50. Politzer P, Jalbout AF, Jin P (2003) Coll Czech Chem Comm 68: 61
51. Jalbout AF, Politzer P (to be published)
52. Benguria R, Lieb EH (1983) Phys Rev Lett 50:1771
53. Bates DR (1991) Adv At Mol Opt Phys 27:1
54. Hati S, Datta D (1996) J Phys Chem 100:4828
55. Politzer P (1980) Isr J Chem 19:224
56. Politzer P (1987) In: March NH, Deb BM (eds) Single-particle density in physics and chemistry. Academic, New York, chap 3
57. March NH (1992) Electron density theory of atoms and molecules. Academic, London, appendix 6.1
58. Parr RG, Donnelly RA, Levy M, Palke WE (1978) J Chem Phys 68:3801
59. Politzer P, Grice ME, Murray JS (2001) J Mol Struct (Theochem) 549:69
60. Wiener JJM, Grice ME, Murray JS, Politzer P (1996) J Chem Phys 104:5109
61. Sen KD, Politzer P (1989) J Chem Phys 90:4370
62. Sen KD, Politzer P (1989) J Chem Phys 91:5123
63. Berkowitz M, Ghosh SK, Parr RG (1985) J Am Chem Soc 107:6811
64. Berkowitz M, Parr RG (1988) J Chem Phys 88:2554
65. Langenaeker W, De Proft F, Geerlings P (1995) J Phys Chem 99:6424
66. Geerlings P, Langenaeker W, De Proft F, Baeten A (1996) In: Murray JS, Sen K (eds) Molecular electrostatic potentials: concepts and applications. Elsevier, Amsterdam, chap 14
67. Jin P, Murray JS, Politzer P (work in progress)