SOME APPROXIMATE ATOMIC AND MOLECULAR ENERGY FORMULAS

Peter POLITZER[1],*, Abraham F. JALBOUT[2] and Ping JIN[3]

*Department of Chemistry, University of New Orleans, New Orleans, LA 70148, U.S.A.;
e-mail:* [1] ppolitze@uno.edu, [2] jalbout@5551@aol.com, [3] pjin@uno.edu

We are pleased and honored to participate in this tribute to Professors Petr Čársky, Ivan Hubač and Miroslav Urban.

We have tested several approximate formulas that relate atomic and molecular energies to the electrostatic potentials at the nuclei, V_0 and $V_{0,A}$, respectively. They are based upon the assumption that the chemical potentials can be neglected relative to V_0 and $V_{0,A}$. Exact, Hartree–Fock and density-functional values were used for the latter. The results are overall encouraging; the errors in the energies generally decrease markedly as the nuclear charges Z increase and the assumptions become more valid. Improvement is needed, however, in fitting the V_0 and $V_{0,A}$ to Z.
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The Hohenberg–Kohn theorem states that the ground-state energy of a system of nuclei and electrons can be expressed rigorously as a functional of its electronic density[1]. In principle, therefore, this remarkable theorem reduces the calculation of the energy from a many-electron to a one-electron problem. It can be argued, however, that this could already be predicted from the much earlier Hellmann–Feynman theorem[2,3]. Indeed the relevant exact relationships have long been known. In this paper, we shall begin by reviewing the derivation of these, and then proceed to investigating an approximate modification of them.

THEORY

For an *N*-electron atom with energy E^{at} and nuclear charge *Z*, the Hellmann–Feynman theorem[2,3] can be written in the form[4–7]

$$\left(\frac{\partial E^{\text{at}}}{\partial Z}\right)_N = V_0 , \tag{1}$$

where V_0 is the electrostatic potential that is produced at the nucleus by the electrons:

$$V_0 = -\int \frac{\rho(\mathbf{r})\,d\mathbf{r}}{r} , \tag{2}$$

in which $\rho(\mathbf{r})$ is the electronic density. Integration of Eq. (1) gives[4,8,9]

$$E^{\text{at}} = \int_{Z'=0}^{Z} [V_0(Z')]_N \, dZ' \tag{3}$$

and subsequent integration by parts yields[8]

$$E^{\text{at}} = 0.5 Z V_0 - 0.5 \int_{Z'=0}^{Z} \left[Z'\left(\frac{\partial V_0(Z')}{\partial Z'}\right) - V_0(Z') \right]_N dZ' \tag{4}$$

or[9]

$$E^{\text{at}} = Z V_0 - \int_{Z'=0}^{Z} \left[Z'\left(\frac{\partial V_0(Z')}{\partial Z'}\right) \right]_N dZ' . \tag{5}$$

Equations (3)–(5) are equivalent exact atomic energy formulas.

The molecular version of Eq. (1) is

$$\left(\frac{\partial E^{\text{mol}}}{\partial Z_A}\right)_{N, Z_{B \neq A}, \{\mathbf{R}_i\}} = V_{0,A} . \tag{6}$$

In Eq. (6), $V_{0,A}$ is the electrostatic potential at nucleus A due to the electrons and other nuclei

$$V_{0,A} = \sum_{B \neq A} \frac{Z_B}{|\mathbf{R}_B - \mathbf{R}_A|} - \int \frac{\rho(\mathbf{r})\,d\mathbf{r}}{|\mathbf{r} - \mathbf{R}_A|} \tag{7}$$

and the $\mathbf{R}_i$ are the nuclear positions. An alternative form of Eq. (6), still invoking the Hellmann–Feynman theorem, can be obtained, following Wilson[10], by scaling the nuclear charges in the molecular Hamiltonian by means of a parameter λ, such that the charge on the i-th nucleus is $Z'_i = \lambda z_i$. In the actual molecule, $\lambda = 1$ and $Z'_i = z_i = Z_i$. Then[10]

$$\left(\frac{\partial E^{\text{mol}}}{\partial \lambda}\right)_{N,\{z_i\},\{\mathbf{R}_i\}} = 2\lambda \sum_A \sum_{B>A} \frac{z_A z_B}{|\mathbf{R}_A - \mathbf{R}_B|} - \sum_A z_A \int \frac{\rho(\mathbf{r},\lambda)\,d\mathbf{r}}{|\mathbf{R}_A - \mathbf{r}|}. \tag{8}$$

Equation (8) differs from Eq. (6) in that all of the nuclear charges are being varied in a concerted fashion, rather than focusing upon a particular one of them. Holding the $\{z_i\}$ and $\{\mathbf{R}_i\}$ fixed and integrating between $\lambda = 0$ and $\lambda = 1$ leads to[8–10]

$$E^{\text{mol}} = \sum_A z_A \int_{\lambda=0}^{1} [V_{0,A}(\lambda)]_N \, d\lambda \tag{9}$$

which can also be written as

$$E^{\text{mol}} = \sum_A \int_{Z'_A=0}^{Z_A} [V_{0,A}(Z'_A)]_N \, dZ'_A . \tag{10}$$

Integration by parts produces[8]

$$E^{\text{mol}} = \sum_A Z_A V_{0,A} - \sum_A \int_{Z'_A=0}^{Z_A} \left[Z'_A \left(\frac{\partial V_{0,A}(Z'_A)}{\partial Z'_A} \right) \right]_N dZ'_A \tag{11}$$

or[9]

$$E^{\text{mol}} = 0.5 \sum_A Z_A V_{0,A} - 0.5 \sum_A \int_{Z'_A=0}^{Z_A} \left[Z'_A \left(\frac{\partial V_{0,A}(Z'_A)}{\partial Z'_A} \right) - V_{0,A} \right]_N dZ'_A . \tag{12}$$

It should be noted, by reference to Eqs (8) and (9), that the $V_{0,A}$ in Eqs (10)–(12) are functions of the simultaneous scaling of the entire set of nuclear charges, not just Z'_A.

Equations (10)–(12) are the molecular analogs of Eqs (3)–(5), and are also exact. A striking feature is that the molecular expressions are formally just

summations over their atomic counterparts; there are no explicit interaction terms. These equations relate atomic and molecular energies rigorously to electrostatic potentials at nuclei and thus to electronic densities. They can therefore be viewed as a manifestation of the Hohenberg–Kohn theorem, linking it to the Hellmann–Feynman.

While Eqs (*3*) and (*10*) might be the easiest of these to apply, Eqs (*4*) and (*11*) have an interesting relationship to the virial theorem[11], according to which

$$E_{at} = 0.5(V_{ne} + V_{ee}) = 0.5ZV_0 + 0.5V_{ee} \qquad (13)$$

and

$$E^{mol} = 0.5(V_{ne} + V_{ee} + V_{nn}) = 0.5\sum_A Z_A V_{0,A} + 0.5(V_{ee} - V_{nn}). \qquad (14)$$

The first terms in Eqs (*13*) and (*14*) are identical to those in Eqs (*4*) and (*11*), which means that the second terms in the latter must equal $-0.5V_{ee}$ and $-0.5(V_{ee} - V_{nn})$, respectively. Since the ratios ZV_0/V_{ee} for atoms and $\sum_A Z_A V_{0,A}/(V_{ee} - V_{nn})$ for molecules have been found to be fairly large in magnitude and roughly constant[6,12–15] at about –6.7, it might be anticipated that reasonably good estimates of atomic and molecular energies could be obtained simply by appropriately scaling the first terms in Eqs (*4*) and (*11*), thus avoiding the difficult integrals. There have been extensive efforts along these lines, with some success, which are reviewed elsewhere[14–18].

Approximate Energy Formulas

A significant problem in directly applying the exact expressions, Eqs (*3*)–(*5*) and (*10*)–(*12*), is the stipulation that the integrations be over isoelectronic series. It has been demonstrated, however, that this requirement can be eliminated by introducing the assumption that the chemical potentials of the systems are zero or negligible[19,20]. These are defined, for atoms and molecules, by[18,21,22]

$$\mu^{at} = \left(\frac{\partial E^{at}}{\partial N}\right)_Z \qquad (15)$$

and

$$\mu^{\text{mol}} = \left(\frac{\partial E^{\text{mol}}}{\partial N}\right)_{\{Z_i\},\{\mathbf{R}_i\}} . \tag{16}$$

The chemical potential has been identified with the negative of the electronegativity[21,22], and is frequently estimated by[21–23]

$$\mu = -0.5(I + A) , \tag{17}$$

where I and A are the ionization potential and electron affinity of the atom or molecule.

To show how μ^{at} is related to the isoelectronic condition in Eqs (3)–(5), write $E^{\text{at}} = E^{\text{at}}(Z,N)$, and thus

$$dE^{\text{at}} = \left(\frac{\partial E^{\text{at}}}{\partial Z}\right)_N dZ + \left(\frac{\partial E^{\text{at}}}{\partial N}\right)_Z dN. \tag{18}$$

Inserting Eqs (1) and (15) and rearranging,

$$\frac{dE^{\text{at}}}{dZ} = V_0 + \mu^{\text{at}}\left(\frac{dN}{dZ}\right) = V_0 + \mu^{\text{at}} , \tag{19}$$

since $dN/dZ = 1$. If it can be assumed that $|\mu^{\text{at}}| << |V_0|$, then

$$\frac{dE^{\text{at}}}{dZ} \approx V_0 . \tag{20}$$

Just as Eq. (1) led *via* integration to the exact atomic energy formulas, Eqs (3)–(5), so does Eq. (20) yield their approximate analogues, Eqs (21)–(23), which do not require that N be held constant:

$$E^{\text{at}} \approx \int_{Z'=0}^{Z} [V_0(Z)]dZ' \tag{21}$$

$$E^{\text{at}} = 0.5ZV_0 - 0.5\int_{Z'=0}^{Z}\left[Z'\left(\frac{\partial V_0(Z')}{\partial Z'}\right) - V_0(Z')\right]dZ' \tag{22}$$

$$E^{\text{at}} = 0.5ZV_0 - \int_{Z'=0}^{Z}\left[Z'\left(\frac{\partial V_0(Z')}{\partial Z'}\right)\right]dZ' . \tag{23}$$

The assumption that $|\mu^{at}| \ll |V_0|$, which is the basis for Eqs (21)–(23), is in general quite a good one. Using Eq. (17), $|\mu| < 0.4$ hartrees for both atoms and molecules[22]. For the hydrogen atom, $|V_0| = 1.0$ hartree but it increases rapidly thereafter, being 5.7 hartrees for lithium, 14.7 hartrees for carbon, 26.5 hartrees for fluorine, *etc.* (Table I)[24].

An analogous procedure will produce the corresponding approximate molecular formulas, Eqs (24)–(26), starting from $E^{mol}(N, \lambda, \{z_i\}, \{\mathbf{R}_i\})$ and taking into account that the $\{z_i\}$ and $\{\mathbf{R}_i\}$ are fixed[19]

$$E^{mol} \approx \sum_A \int_{Z'_A = 0}^{Z_A} [V_{0,A}(Z'_A)] dZ'_A \qquad (24)$$

$$E^{mol} \approx \sum_A Z_A V_{0,A} - \sum_A \int_{Z'_A = 0}^{Z_A} \left[Z'_A \left(\frac{\partial V_{0,A}(Z'_A)}{\partial Z'_A} \right) \right] dZ'_A \qquad (25)$$

TABLE I
Calculated values of V_0 (in hartrees)

Atom	Z	WS(exact)[a]	B3LYP[b]	HF[b]
Li	3	–5.7183	–5.71815	–5.71541
Be	4	–8.4273	–8.41909	–8.40710
B	5	–11.395	–11.39513	–11.37992
C	6	–14.702	–14.70448	–14.68954
N	7	–18.3393	–18.34596	–18.33498
O	8	–22.2623	–22.26596	–22.25225
F	9	–26.5181	–26.51879	–26.50939
Ne	10	–31.1101	–31.10300	–31.09973
Na	11	–35.4375	–35.42779	–35.41570
Mg	12	–39.9368	–39.92694	–39.90806
Al	13	–44.5202	–44.51611	–44.49595
Si	14	–49.2658	–49.25938	–49.24102
P	15	–54.1667	–54.16334	–54.14772
S	16	–59.2005	–59.19691	–59.17941
Cl	17	–64.39406	–64.35116	–64.37297
Average absolute error		–	0.0072	0.0163

[a] Ref.[24]; [b] ref.[14]

$$E^{\text{mol}} \approx 0.5 \sum_{\text{A}} Z_{\text{A}} V_{0,\text{A}} - 0.5 \sum_{\text{A}} \int_{Z'_{\text{A}}=0}^{Z_{\text{A}}} \left[Z'_{\text{A}} \left(\frac{\partial V_{0,\text{A}}(Z'_{\text{A}})}{\partial Z'_{\text{A}}} \right) - V_{0,\text{A}} \right] \text{d}Z'_{\text{A}} . \qquad (26)$$

The $|\mu^{\text{mol}}| << |V_{0,\text{A}}|$ assumption is generally valid, since $|\mu^{\text{mol}}| < 0.4$ [22] and the $|V_{0,\text{A}}|$ are very close to their values in the corresponding free atoms[14,16].

If μ^{at} and μ^{mol} were zero, then Eq. (*20*) and its molecular counterpart would be rigorously correct, as would Eqs (*21*)–(*26*). In Thomas–Fermi theory (which becomes exact as the total nuclear charge approaches infinity[25]), μ^{at} does equal zero[22,26,27]. It has been speculated by Komorowski[28] and by Ganguly[29,30] that this may in fact be true in general for both atoms and molecules at equilibrium; Ganguly has suggested that μ^{at} and μ^{mol} become non-zero in interactive situations[29].

Since there are no *N*-related restrictions upon the paths of integration in the approximate Eqs (*21*)–(*26*), these can be chosen, for convenience, to be the neutral systems, *i.e.* $N = Z$ for atoms and $\sum_{\text{A}} Z_{\text{A}}$ for molecules. Initial limited tests of this approach were carried out some time ago; Hartree–Fock values of V_0 and $V_{0,\text{A}}$ for neutral atoms[8] and homonuclear diatomic molecules[19], which are known to be accurate through second-order[31,32], were fit to three-term power series in $Z^{1/3}$ and $Z_{\text{A}}^{1/3}$ and then used in Eqs (*22*) and (*26*) to calculate E^{at} and E^{mol}. The results, even for a few heteronuclear diatomics[19], were encouraging. A similar procedure was subsequently applied to the neutral atoms Li–Cl [20], using Eq. (*21*) and expressing exact, Hartree–Fock and density-functional V_0 as $\sum_{i=0}^{4} \alpha_i Z^i$. This produced errors of roughly 2% for very low Z, decreasing to about 0.6% for $Z = 15$–17, with the Hartree–Fock being slightly worse than the others.

In the present work, we have investigated some modifications of the procedure recently applied to the atoms[20]. We have also treated molecules, at a higher computational level than before[19], taking a group of homonuclear diatomics as the basis for establishing $V_{0,\text{A}}(Z_{\text{A}})$ relationships.

PROCEDURE AND RESULTS

Atoms

Exact V_0 values for the atoms Li–Cl are available from Wang and Smith[24]. We have shown that these are reproduced with good accuracy by three different density-functional techniques[14,20]: B3LYP, B3PW91 and B3P86. These involve Becke's three-parameter hybrid (B3)[33] in conjunction with the Lee–Yang–Parr (LYP)[34], the Perdew–Wang-91 (PW91)[35] and the Perdew-86 (P86)[36]

correlation expressions. The basis set was the 6-311+G(3df). The average errors are about 0.007 hartrees, less than half of the Hartree–Fock (HF)[14,20]. The B3LYP and the HF V_0 are listed in Table I, along with the Wang–Smith (WS); the B3PW91 and the B3P86 are very similar to the B3LYP, and are accordingly not included in this table.

In our earlier study[20], we fit the data in Table I (as well as the B3PW91 and B3P86 V_0) to power series of the form

$$V_0 = \alpha_0 + \alpha_1 Z + \alpha_2 Z^2 + \alpha_3 Z^3 + \alpha_4 Z^4 \tag{27}$$

and inserted these into Eq. (*21*) to obtain atomic energies. The intercepts α_0 should ideally be zero, since V_0 must equal zero for $Z = 0$. Accordingly, in order to make $|\alpha_0|$ smaller, we added the point $Z = 0$, $V_0 = 0$ to each of the five databases. As a consequence, each $|\alpha_0|$ was less than 0.05 hartrees. Another possibility, which we now examine, is not to include the hypothetical $Z = 0$, $V_0 = 0$ and to accept that the $|\alpha_0|$ will be larger than desired. We also tested an alternative power series, Eq. (*28*):

$$V_0 = \beta_1 Z^{1/3} + \beta_2 Z^{2/3} + \beta_3 Z^{3/3} + \beta_4 Z^{4/3} \ . \tag{28}$$

The problem of a non-zero intercept does not arise with Eq. (*28*). We will present the results for the WS and the B3LYP V_0.

In Table II are the approximate atomic energy expressions produced from the fitted V_0 relationships, Eqs (*27*) and (*28*), in conjunction with Eq. (*21*). We have used the latter because it is easier to apply than Eqs (*22*) and (*23*). It can be seen that not including the point $Z = 0$, $V_0 = 0$ increases the magnitude of α_0 (the coefficient of Z in Table II) from less than 0.05 to about 2.3 hartrees.

The equations in Table II yield the energies listed in Table III, where they are compared to Wang and Smith's exact non-relativistic values. Several general observations can be made:

1. The WS and the B3LYP V_0 give very similar results.

2. The percent error decreases as Z becomes larger.

3. Most interesting is the effect of the point $Z = 0$, $V_0 = 0$. When it is included (the A columns in Table III), the calculated energies are uniformly slightly too positive, with percent errors in the neighborhood of 2% for very low Z but decreasing to about 0.6% as Z approaches 17; however the

magnitudes of the errors consistently increase as Z becomes larger. When $Z = 0$, $V_0 = 0$ is not included (the B and C columns), the energies are invariably too negative, with per cent errors that are initially very high but diminish rapidly to about 0.1% for the WS, B and B3LYP, B values; what is particularly pleasing is that the magnitudes of the errors also decrease as Z increases.

4. In comparing the two sets of results that were obtained without explicitly involving $Z = 0$, $V_0 = 0$ (the B and C columns), it is seen that the errors are smaller for the power series in Z, Eq. (*27*), than for that in $Z^{1/3}$, Eq. (*28*).

Molecules

We created a molecular database by computing[37], at the HF/6-311+G(3df) and B3LYP/6-311+G(3df) levels, the $V_{0,A}$ for each of a series of twelve homonuclear diatomic molecules (Table IV), using their experimental equilibrium bond lengths R_e [38,39]. Comparison of Tables I and IV confirms our earlier statement that the $V_{0,A}$ are very similar to the V_0 of the corresponding free atoms; this is true in general[14,16], not just for homonuclear diatomics.

The data in Table IV were fit to power series in both Z_A and $Z_A^{1/3}$, analogous to Eqs (*27*) and (*28*), which were then used in Eq. (*24*) to generate the molecular energy expressions in Table V. The point $Z_A = 0$, $V_{0,A} = 0$ was not

TABLE II
Approximate atomic energy relationships

Source of V_0		Equation
WS	A.	$E^{at} = -3.28676 \times 10^{-5}Z^5 + 0.00258700Z^4 - 0.0958697Z^3 - 0.536835Z^2 - 0.0466951Z$ Z = 0, V$_0$ = 0 included[a]
	B.	$E^{at} = -1.00792 \times 10^{-4}Z^5 + 0.00611885Z^4 - 0.164172Z^3 + 0.0641640Z^2 - 2.38097Z$ Z = 0, V$_0$ = 0 not included
	C.	$E^{at} = 0.290068Z^{7/3} - 7.01294Z^{6/3} + 17.5822Z^{5/3} - 14.3389Z^{4/3}$
B3LYP	A.	$E^{at} = -3.17760 \times 10^{-5}Z^5 + 0.00254673Z^4 - 0.0953560Z^3 - 0.539205Z^2 - 0.0446012Z$ Z = 0, V$_0$ = 0 included[a]
	B.	$E^{at} = -0.966774 \times 10^{-4}Z^5 + 0.00592145Z^4 - 0.160621Z^3 + 0.0350779Z^2 - 2.27511Z$ Z = 0, V$_0$ = 0 not included
	C.	$E^{at} = 0.302499Z^{7/3} - 7.09122Z^{6/3} + 17.7481Z^{5/3} - 14.4583Z^{4/3}$

[a] Ref.[20]

TABLE III
Approximate atomic energies (in hartrees), from relationships in Table II, compared to exact non-relativistic values. Per cent errors are in parentheses

Atom	Z	WS, A[a]	WS, B	WS, C	B3LYP, A[a]	B3LYP, B	B3LYP, C	Exact[b]
Li	3	−7.359 (1.59)	−10.527 (40.8)	−11.675 (56.1)	−7.363 (1.54)	−10.390 (38.9)	−11.699 (56.4)	−7.478
Be	4	−14.283 (2.62)	−17.541 (19.6)	−18.669 (27.3)	−14.289 (2.58)	−17.402 (18.6)	−18.691 (27.4)	−14.667
B	5	−24.124 (2.15)	−27.313 (10.8)	−28.466 (15.5)	−24.130 (2.13)	−27.177 (10.2)	−28.487 (15.5)	−24.654
C	6	−37.217 (1.66)	−40.291 (6.46)	−41.493 (9.64)	−37.222 (1.65)	−40.160 (6.12)	−41.513 (9.69)	−37.845
N	7	−53.856 (1.34)	−56.836 (4.12)	−58.080 (6.40)	−53.860 (1.34)	−56.707 (3.88)	−58.099 (6.43)	−54.589
O	8	−74.297 (1.03)	−77.237 (2.89)	−78.492 (4.56)	−74.298 (1.03)	−77.108 (2.72)	−78.512 (4.59)	−75.068
F	9	−98.760 (0.98)	−101.719 (1.99)	−102.947 (3.22)	−98.759 (0.98)	−101.585 (1.86)	−102.968 (3.24)	−99.734
Ne	10	−127.437 (1.16)	−130.456 (1.18)	−131.630 (2.09)	−127.433 (1.17)	−130.318 (1.07)	−131.651 (2.10)	−128.938
Na	11	−160.490 (1.09)	−163.586 (0.82)	−164.698 (1.51)	−160.484 (1.09)	−163.442 (0.73)	−164.719 (1.52)	−162.255
Mg	12	−198.062 (1.00)	−201.221 (0.58)	−202.288 (1.12)	−198.054 (1.00)	−201.072 (0.51)	−202.306 (1.13)	−200.053
Al	13	−240.274 (0.85)	−243.458 (0.46)	−244.519 (0.90)	−240.264 (0.86)	−243.306 (0.40)	−244.533 (0.90)	−242.346
Si	14	−287.235 (0.73)	−290.392 (0.36)	−291.498 (0.74)	−287.220 (0.74)	−290.237 (0.30)	−291.504 (0.74)	−289.359
P	15	−339.040 (0.65)	−342.131 (0.26)	−343.318 (0.60)	−339.018 (0.66)	−341.971 (0.21)	−343.313 (0.60)	−341.259
S	16	−395.782 (0.58)	−398.802 (0.17)	−400.064 (0.49)	−395.745 (0.59)	−398.631 (0.13)	−400.043 (0.49)	−398.110
Cl	17	−457.545 (0.57)	−460.568 (0.09)	−461.813 (0.36)	−457.484 (0.58)	−460.373 (0.05)	−461.769 (0.35)	−460.148

[a] Ref.[20]; [b] ref.[24]

included in this process. The resulting energies are listed in Table VI. For comparison, the estimated exact values are given for seven of the molecules[15].

Overall, the trends in the calculated molecular energies (Table VI) are similar to those observed for the atoms (Table III) when $Z = 0$, $V_0 = 0$ is not included. They are generally too negative, particularly those produced by the power series in $Z_A^{1/3}$ (B columns), but for the most part, both the

TABLE IV
Calculated values of $V_{0,A}$ (in hartrees)

Molecule	Z_A	B3LYP	HF
Li_2	3	–5.745868	–5.742607
B_2	5	–11.396923	–11.325013
C_2	6	–14.696317	–14.645001
N_2	7	–18.317584	–18.267011
O_2	8	–22.230116	–22.180452
F_2	9	–26.492993	–26.459216
Na_2	11	–35.442905	–35.428542
Al_2	13	–44.519083	–44.448244
Si_2	14	–49.261617	–49.229822
P_2	15	–54.172167	–54.137770
S_2	16	–59.197615	–59.155811
Cl_2	17	–64.344178	–64.356902

TABLE V
Approximate molecular energy relationships

Source of $V_{0,A}$		Equation
B3LYP	A.	$E^{mol} = 2[-0.818028 \times 10^{-4}Z_A^5 + 0.00520012Z_A^4 - 0.148270Z_A^3 - 0.0540361Z_A^2 - 1.978846Z_A]$
	B.	$E^{mol} = 2[0.268404Z_A^{7/3} - 6.91037Z_A^{6/3} + 17.4606Z_A^{5/3} - 14.3216Z_A^{4/3}]$
HF	A.	$E^{mol} = 2[-0.954709 \times 10^{-4}Z_A^5 + 0.00588810Z_A^4 - 0.161227Z_A^3 + 0.0574577Z_A^2 - 2.36163Z_A]$
	B.	$E^{mol} = 2[0.285699Z_A^{7/3} - 7.06173Z_A^{6/3} + 17.8866Z_A^{5/3} - 14.7006Z_A^{4/3}]$

percents and the magnitudes of the errors become much smaller as Z_A becomes larger. Unfortunately, the sequences of energies in the A columns, obtained from the power series in Z_A, intersect the exact values at about Si_2, and then continue to increasingly err in the positive direction.

DISCUSSION AND CONCLUSIONS

It is to be anticipated that the approximate atomic and molecular energies will improve with higher Z and Z_A, as the assumptions $|\mu^{at}| << |V_0|$ and $|\mu^{mol}| << |V_{0,A}|$, upon which Eqs (*21*) and (*24*) are based, gain validity. Superposed upon this factor, however, is the key issue of how well the V_0 and $V_{0,A}$ are represented by the various fitted equations. The energies are extremely sensitive to this. For example, including the point $Z = 0$, $V_0 = 0$

TABLE VI
Approximate molecular energies (in hartrees), from relationships in Table V. Some exact values are given. Per cent errors are in parentheses

Molecule	Z_A	B3LYP, A	B3LYP, B	HF, A	HF, B	Exact[a]
Li_2	3	−20.050	−23.433	−20.934	−23.671	
B_2	5	−53.569	−56.914	−54.287	−57.027	
C_2	6	−79.483	−82.874	−80.075	−82.894	−75.923
		(4.69)	(9.16)	(5.47)	(9.18)	
N_2	7	−112.491	−115.933	−112.968	−115.850	−109.542
		(2.69)	(5.83)	(3.13)	(5.76)	
O_2	8	−153.168	−156.626	−153.549	−156.436	−150.328
		(1.89)	(4.19)	(2.14)	(4.06)	
F_2	9	−201.976	−205.397	−202.281	−205.101	−199.530
		(1.23)	(2.94)	(1.38)	(2.79)	
Na_2	11	−325.385	−328.614	−325.573	−328.122	
Al_2	13	−484.917	−488.003	−484.968	−487.349	
Si_2	14	−578.751	−581.858	−578.714	−581.140	
P_2	15	−682.230	−685.421	−682.101	−684.648	−682.703
		(0.07)	(0.40)	(0.09)	(0.28)	
S_2	16	−795.580	−798.865	−795.377	−798.050	−796.383
		(0.10)	(0.31)	(0.13)	(0.21)	
Cl_2	17	−919.073	−922.348	−918.850	−921.502	−920.389
		(0.14)	(0.21)	(0.17)	(0.12)	

[a] Ref.[15]

causes positive shifts of the E^{at} sufficient to make all of them too high, whereas omitting $Z = 0$, $V_0 = 0$ makes them all too low. A similar situation was observed at the molecular level. When H_2 is part of the database, the E^{mol} are significantly more positive than without it.

A consistent feature of all of our calculated energies is that, for each $E^{at}(Z)$ or $E^{mol}(Z_A)$ expression, the quantity $E_{calc} - E_{exact}$ becomes more positive as Z or Z_A increases. It would of course be most desirable that this quantity approach zero. Thus while the present results are viewed as encouraging, in terms of the accuracy that is achieved at the higher Z and Z_A, it is clear that more work is needed. One option is to eliminate from the databases the V_0 and $V_{0,A}$ corresponding to low Z and Z_A, for which the $|\mu^{at}| < |V_0|$ and $|\mu^{mol}| \ll |V_{0,A}|$ assumptions are poorest, and to extend them to higher Z and Z_A. Other $V_0(Z)$ and $V_{0,A}(Z_A)$ representations should also be tested, for example longer power series or perhaps quite different functional forms. Such studies are planned.

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