On the Partitioning of Energy for Atoms, Ions, and Molecules

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The fact that, for neutral atoms, the interelectronic repulsion energy I is a constant fraction ($\sim 1/3$) of the total energy E is discussed in the light of several approximate energy formulas, theoretical and empirical. We then derive the asymptotic form of the non-relativistic energy of a neutral atom as $E = -kZ^{7/3}$ a.u. ($Z =$ atomic number) with k probably between $\dfrac{1}{2}\left(\dfrac{3}{2}\right)^{1/3}$ and $\dfrac{9}{14}\left(\dfrac{3}{2}\right)^{1/3}$. For $6 \leq Z \leq 90$, the actual energies are in fact between these limits, while the formula implies $I/E = 1/3$. The ratio of interelectronic repulsion energy to total electronic energy for ions and molecules is derived.

Mit der Hilfe einiger theoretischer und empirischer Näherungsformeln wird die Tatsache diskutiert, daß für neutrale Atome die zwischenelektronische Abstoßungsenergie I stets etwa 1/3 der elektronischen Gesamtenergie E beträgt. Die asymptotische Form der nicht relativistischen Energie eines neutralen Atoms wird dann zu $E = -kZ^{1/3}$ abgeleitet, wobei Z die Kernladungszahl ist und k wahrscheinlich zwischen $\dfrac{1}{2}\left(\dfrac{3}{2}\right)^{1/3}$ und $\dfrac{9}{14}\left(\dfrac{3}{2}\right)^{1/3}$ liegt. Für $6 \leq Z \leq 90$ liegen die berechneten Energien tatsächlich innerhalb dieser Grenzen. Gleichzeitig enthält diese Formel das Verhältnis $I/E = 1/3$. Ferner wird das Verhältnis von I zu E für Ionen und Moleküle abgeleitet.

Nous discutons le fait que, pour les atomes neutres, l'énergie de répulsion interélectronique I est toujours à peu près 1/3 de l'énergie électronique totale E. Après avoir examiné le rapport entre ce fait et certaines formules théoriques et empiriques pour l'énergie, nous démontrons que la forme asymptotique de l'énergie est $E = -kZ^{7/3}$ u.a. ($Z =$ charge du noyau), avec k probablement entre $\dfrac{1}{2}\left(\dfrac{3}{2}\right)^{1/3}$ et $\dfrac{9}{14}\left(\dfrac{3}{2}\right)^{1/3}$. Les énergies calculées pour $6 \leq Z \leq 90$ sont en accord avec cette règle. La formule $E = -kZ^{7/3}$ conduit aussi à $I/E = 1/3$. Nous démontrons également le rapport entre I et E pour les ions et les molécules.

Several years ago, Fraga [1] pointed out an interesting regularity in atomic structure calculations. For the ground and lower excited states of neutral atoms and negative ions, the expectation value of the interelectronic interaction is in a constant ratio to the total electronic energy, the magnitude of the ratio being slightly above 1/3, which was suggested as a theoretical value. Gáspár [2] has given some further discussion of this point. Actually, the energies and expectation values for all terms from a given configuration differ only slightly, so if the rule is fulfilled approximately for the ground term, it is automatically fulfilled for the others. Thus, we shall discuss only the lowest term for a configuration in what follows.

Writing the total energy as E, the interelectronic repulsion energy as I, the kinetic energy as T, and the electron-nuclear attraction energy as A, we have

$$E = I + A + T \tag{1}$$

and, by the virial theorem,

$$T = -E = -1/2(I + A). \qquad (2)$$

From these relations, one sees that $I/E = -1/3$ implies $A/E = 7/3$. The Hellmann-Feynman Theorem [3, 4] gives

$$A = Z(\partial E/\partial Z)_N \qquad (3)$$

where Z is the nuclear charge and the number of electrons N is to be held constant in the differentiation.

We also note that, for N fixed, the energy can be written as a function of Z in the well-known expansion [4]

$$E = W_2 Z^2 + W_1 Z + W_0 + W_{-1} Z^{-1} + \cdots. \qquad (4)$$

Here, W_2 is the sum of the eigenvalues of the N lowest hydrogenic orbitals, and W_1 is the expectation value of $\sum 1/r_{ij}$ for the determinantal wavefunction formed from these (in the case of degeneracy, W_1 is a root of a secular equation). Thus, W_2 is necessarily negative and W_1 necessarily positive. From Eqs. (4) and (3), one has $A/E = 2 - (W_1/W_2) Z^{-1} +$ terms in Z^{-2}, suggesting A/E something above 2. Now $Z W_1$ is essentially I and $Z^2 W_2$ is $T + A$, if we can neglect contributions contained in W_0, so $(W_1/W_2) Z^{-1} \approx I/(T + A)$. Using the virial theorem, Eq. (2), we obtain the following relation for $\alpha = A/E$:

$$\alpha = 2 - (2 - \alpha)/(-1 + \alpha).$$

The solution is $\alpha = 2$, so the deviation of the true ratio from 2 is a measure of the importance of the second-order terms in W_0.

Now if $E(Z)$ for N fixed goes as CZ^r, (3) gives $A = rE$, and $I = (2 - r) E$, etc. Fraga [1] noted that the Thomas-Fermi theory [5] for neutral atoms predicts

$$E = -0.7687 \, Z^{7/3} \quad \text{a.u.} \qquad (5)$$

which, with (3), gives $A/E = 7/3$. We shall ignore the fact that this and subsequent formulas refer to $E(Z)$ for $N = Z$ and not for fixed N, and return to this point later. The Thomas-Fermi theory cannot, however, be used to justify the constancy of A/E, I/E, etc., since the formula (5) is known to be in error by 20–30%, even for the heavier atoms. Further, the theory gives no stable solutions for negative ions. The errors are due to neglect of exchange and to the breakdown, for distances very close to and very far away from the nucleus, of the assumptions of the theory. The breakdown close to the nucleus, where the potential energy is large, is most serious for energy calculations.

Scott [6] has shown how Eq. (5) may be corrected for exchange and the rapidly varying (Coulombic) field near the nucleus. His formula gave quite good agreement with experimentally and theoretically determined energies. It was further modified by March and Plaskett [7], who gave:

$$E(\text{a.u.}) = -0.7687 \, Z^{7/3} + \tfrac{1}{2} Z^2 - 0.266 \, Z^{5/3} + O(Z^{4/3}), \qquad (6)$$

in even better agreement. By differentiation of (6)

$$\frac{Z}{E} \frac{dE}{dZ} = \frac{7}{3} + 0.217 \, Z^{-1/3} - 0.372 \, Z^{-2/3} + \cdots.$$

The ratio A/E should then be slightly above $7/3$, as Fraga's tables show.

In fact Foldy [8], considering the energies of neutral atoms calculated by the Hartree method, concluded that a good fit could be obtained by $E = -13.6 Z^{12/5}$ eV. Scott [6] has discussed the relation between his and Foldy's formulas. Now the latter implies $A/E = 12/5$ and $I/E = -2/5$, which is in better agreement with the numbers in Fraga's Tables 1 and 2 than $7/3$ and $-1/3$.

We will now show that, for neutral atoms, the leading term in $E(Z)$ goes as $Z^{7/3}$, independently of the Thomas-Fermi theory. First, for large atomic number, the coefficient W_2 in the expansion (4) goes as $Z^{1/3}$. We can write

$$W_2(\text{a.u.}) = \sum_\alpha q_\alpha(-1/2n_\alpha^2)$$

where q_α is the occupation number of the orbital α with principal quantum number n_α, so $\sum_\alpha q_\alpha = N$. We can get an idea of the overall E vs. N dependence of W_2 by considering only closed shells, where orbitals with principal quantum number n_α up to and including n_m are filled. Thus, going over to sums over principal quantum numbers,

$$W_2(\text{a.u.}) = -\tfrac{1}{2} \sum_{n_\alpha} 2n_\alpha^2/n_\alpha^2 = -n_m \tag{7}$$

and

$$N = \sum_{n_\alpha} 2n_\alpha^2 = \tfrac{1}{3} n_m(n_m + 1)(2n_m + 1) \tag{8}$$

where we have used

$$\sum_{l=1}^{n-1} 2(2l+1) = 2n^2 .$$

Now (8) can be inverted to give the asymptotic series

$$n_m = \left(\frac{3}{2}\right)^{1/3} Z^{1/3} - \frac{1}{2} Z^0 + \frac{(3/2)^{1/3}}{12} Z^{-1/3} + O(Z^{-5/3}) . \tag{9}$$

Thus W_2 goes as $Z^{1/3}$, which makes E go as $Z^{7/3}$ for neutral atoms $(N = Z)$, but with a coefficient fifty per cent higher than that of (5), which is already much too high. As mentioned above, $Z W_1$, which is of opposite sign, must also go as $Z^{4/3}$. Gáspár [2] also indicated that W_1/Z and W_2 had the same Z-dependence. He estimated it as $Z^{0.40}$ from results of direct calculation for atom with $Z \geq 3$ and noted that the exponent decreased when systems of higher atomic number were considered (for atoms with $Z \geq 10$, he gives $Z^{0.38}$).

If we again take $Z^2 W_2$ as approximately $T + A$ and $Z W_1$ as approximately I, the fact that the ratios of T/E, A/E, and I/E are constants independent of Z means the terms are proportional. Putting $Z W_1 = \alpha Z^{7/3}$, we must have $-(3/2)^{1/3} + \alpha = -0.769$ to agree with the Thomas-Fermi result, or $\alpha = 0.386$, which means $I/(T + A) = -0.334$. For $A/E = 7/3$, this would be $-1/4$, while $A/E = 12/5$ makes this $-2/7$. Deviations again indicate the importance of W_2 terms. Note that the virial theorem applies to W_2, and gives $T = -\tfrac{1}{2} A$ in this approximation.

We now go on to a direct estimation of W_1. For a closed shell, the zero-order function is non-degenerate, simplifying the calculation. We ignore exchange, which comes in as a lower power of Z in the Thomas-Fermi theory and as a lower

power of the density for the electron gas. Then

$$W_1 = 2 \sum_{n_i=1}^{n_m} \sum_{l_i < n_i} (2l_i + 1) \sum_{n_j=1}^{n_m} \sum_{l_j < n_j} (2l_j + 1)$$
$$\times \int dr_1 \, dr_2 \, |u_{n_i l_i}(r_1)|^2 \, |u_{n_j l_j}(r_2)|^2 \, r_>^{-1} \qquad (10)$$

where $u_{nl}(r)$ is the hydrogenic radial function and $r_>$ is the greater of r_1 and r_2. Let us first consider terms for $n_j < n_i$. The most probable value of r for $u_{nl}(r)$ increases with n, indeed

$$\int |u_{nl}(r)|^2 \, r^{-1} \, dr = n^{-2},$$

and $\langle r \rangle_{nl} > \langle r \rangle_{n'l'}$ for $n > n'$ independently of l and l' as long as $n < 7$. Then we may put $r_> = r_1$, and

$$\int dr_1 \, dr_2 \, |u_{n_i l_i}(r_1)|^2 \, |u_{n_j l_j}(r_2)|^2 \, r_>^{-1} = \int dr_1 \, |u_{n_i l_i}(r_1)|^2 \, r_1^{-2} = n_i^{-2},$$

so the terms with $n^i > n_j$ contribute

$$2 \sum_{n_i=1}^{n_m} \sum_{n_j=1}^{n_i-1} \sum_{l_i < n_i} (2l_i + 1) \sum_{l_j < n_j} (2l_j + 1) \, n_i^{-2}$$
$$= 2 \sum_{n_i=1}^{n_m} \sum_{n_j=1}^{n_i-1} n_j^2 = \frac{1}{3} \sum_{n_i=1}^{n_m} (n_i - 1) (n_i) (2n_i - 1)$$
$$= \frac{1}{6} n_m^2 (n_m + 1) (n_m - 1)$$

and likewise for the terms with $n_i < n_j$. For the remaining terms $(n_i = n_j)$ in W_1, we assume that for $l_i > l_j \, r_>$ may be put equal to r_1 in the integral of Eq. (10), although this approximation is expected to be less accurate than that made above for $n_i \neq n_j$. Then

$$\int dr_1 \, dr_2 \, |u_{n_i l_i}(r_1)|^2 \, |u_{n_i l_j}(r_2)|^2 \, r_>^{-1} = n_i^{-2}$$

independently of j. If we now also use this for the case $l_i = l_j$, we may sum the contribution of the $n_i = n_j$ terms to W_1:

$$2 \sum_{n_i=1}^{n_m} \sum_{l_i=1}^{n_i-1} (2l_i + 1) \sum_{l_j=1}^{n_i-1} (2l_j + 1) \, n_i^{-2} = \sum_{n_i=1}^{n_m} \sum_{l_i=1}^{n_i-1} 2(2l_i + 1) = N. \qquad (11)$$

For the neutral atom, these terms give a contribution to the energy going as Z^2.

The leading term in Z from W_1 is then $\frac{1}{3} n_m^4 = \frac{1}{2} \left(\frac{3}{2} \right)^{1/3} Z^{4/3}$, contributing $\frac{1}{2} \left(\frac{3}{2} \right)^{1/3} Z^{7/3}$ to the energy. Combining this with the contribution of W_2, we have

$$E = -\frac{1}{2} \left(\frac{3}{2} \right)^{1/3} Z^{7/3} = -15.6 \, Z^{7/3} \quad \text{eV}. \qquad (12a)$$

We do not anticipate that the approximations used are sufficiently good to predict higher order terms in Z in the expansion. The magnitude of E from (12a) is generally too low, since we have not considered W_0, while our previous arguments show that it contains an appreciable term in $Z^{7/3}$. The calculation of W_0

presents much more difficulty, as it is a sum of pair energies, each of which is obtained from solution of a two-electron inhomogeneous differential equation. The structure and calculation of W_0 has been discussed by Layzer and co-workers [9].

Layzer [9b] has also proposed a simple screening theory which we use, first in extremely crude form, to estimate the $Z^{7/3}$ term in W_0. We suppose that the effect of interelectronic repulsion can be approximated by imagining all the electrons to be in hydrogenic orbitals with some effective principal quantum number $\bar{n}$ and some effective charge $Z - \bar{s}Z$, so $\bar{s}$ is a screening constant. Then we equate $W_2 Z^2 + W_1 Z + W_0$ to the hydrogenic formula $-N(Z - \bar{s}Z)^2/(2\bar{n}^2)$ and put $W_2 = -n_m$ and $W_1 = \frac{1}{3}n_m^4$. We find $N/\bar{n}^2 = 2n_m/Z^2$ and $\bar{s} = \frac{1}{6}n_m^3$, so

$$W_0 = -N\bar{s}^2 Z^2/(2\bar{n}^2) = -n_m^7/36 .$$

Adding this to (12a), we obtain

$$E = -\frac{9}{16}\left(\frac{3}{2}\right)^{1/3} Z^{7/3} = -17.52\,Z^{7/3} \quad \text{eV} \tag{12b}$$

which is in fairly good agreement with the experimental values [8]. The next approximation is to consider each principal quantum number separately. The energy difference between the system with all shells through the n-shell, and with all shells through the $(n-1)$-shell, filled (keeping leading terms only) is supposed to be given by the energy of $2n^2$ non-interacting electrons with effective principal quantum number $\bar{n}_n$ moving in the field of a nucleus of effective charge $Z(1 - \bar{s}_n)$. Equating the two expressions we find $\bar{n}_n$ and $\bar{s}_n$, and then the contribution to W_0, W_{0n}:

$$-Z^2 + \frac{1}{3}Z(4n^3) + W_{0n} = -(n/\bar{n}_n)^2\,(Z^2 - 2\bar{s}_n Z^2 + \bar{s}_n^2 Z^2) .$$

Thus $\bar{n}_n = n$, $\bar{s}_n = 2n^3 Z$, and $W_{0n} = -\frac{4}{9}n^6$, so that

$$W_0 = \sum_{n=1}^{n_m} W_{0n} = -\frac{4}{9}\left(\frac{n_m^7}{7} + \frac{n_m^6}{2} + \cdots\right)$$

which, added to (12a), gives

$$E = -\frac{9}{14}\left(\frac{3}{2}\right)^{1/3} Z^{7/3} = -20.02\,Z^{7/3} \quad \text{eV} . \tag{12c}$$

Results from bare-nucleus perturbation theory calculations indicate that the formula (12a), which includes zero-order and first-order terms, should be too high, while (12c), in which second-order terms appear, should be too low, but closer to the correct value. In Fig. 1, formulas (12a) and (12c) are compared with experimental values given by Foldy [8] for neutral atoms with $Z = 6, 7, 8, 10, 20, 30, 40, 50, 60, 70, 80$, and 90. The energies all fall between the two curves.

Actually, it is a little surprising that such good accuracy is obtained from the $Z^{7/3}$ terms in the energy, since the coefficient of the terms in Z^2 need not be negligible, and $Z^{-1/3}$ goes from $\frac{1}{2}$ to $\frac{1}{5}$ as Z goes from 10 to 100. The accuracy of formula (12c) implies cancellation between different contributions to the Z^2 term. For example, the term in W_1 due to interactions of electrons in the same shell
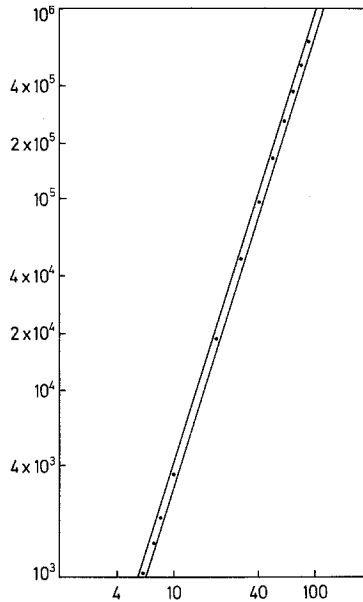
Fig. 1. Energy of neutral atoms (negative value in atomic units) vs. atomic number. Points are Hartree results given by Foldy [8], upper line is Eq. (12c), lower line is Eq. (12a)

(Eq. (11)) is exactly cancelled by a term of the same order in Z in $\frac{1}{3}n_m^4$, with n_m given by Eq. (9).

As mentioned above, in using the formulas for $E(Z)$ for neutral atoms in (3), we are ignoring the difference between dE/dZ along the line $N = Z$ in the N, Z plane and along the line $N = $ constant. We shall denote the former quantity by $(dE/dZ)_{\text{neutral}}$. The difference between these two quantities is essentially an ionization potential, and it is well known that the first ionization potential of a neutral atom is essentially Z-independent and thus becomes small compared to the total energy and $(dE/dZ)_{\text{neutral}}$. Thus our replacing $(\partial E/\partial Z)_N$ by $(dE/dZ)_{\text{neutral}}$ was justified. Specifically, we have

$$(dE/dZ)_{\text{neutral}} = \left(\frac{\partial E}{\partial N}\right)_Z + \left(\frac{\partial E}{\partial Z}\right)_N.$$

Now $(\partial E/\partial N)_Z$ is somewhere between the ionization potential and the electron affinity of the neutral atom of atomic number Z, and may be neglected. Alternatively, note that E as a function of Z for N fixed is given by Eq. (4), with $W_2 = -\left(\frac{3}{2}\right)^{1/3} N^{1/3}$, $W_1 = \frac{1}{2}\left(\frac{3}{2}\right)^{1/3} N^{4/3}$, and $W_0 = -\frac{1}{7}\left(\frac{3}{2}\right)^{1/3} N^{7/3}$. Thus we can write directly

$$\alpha = \frac{A}{E} = \frac{Z}{E}\left(\frac{\partial E}{\partial Z}\right)_N = \frac{2Z^2 W_2 + Z W_1}{Z^2 W_2 + Z W_1 + W_0} = \frac{7}{3}.$$

The relative smallness of ionization potentials implies that the dependence of energy on Z and its consequences for the partitioning of the energy should hold

approximately for negative and positive ions as well as for neutral atoms. The energy of the singly negative ion differs from that of the neutral by an electron affinity, that of the singly positive ion from a neutral by an ionization potential. Ionization potentials being generally larger than electron affinities, the ration A/E for ions of a single negative charge should be closer to the ratio for neutral atoms than should A/E for ions of single positive charge.

If one now considers ions with more than one positive charge, the ratio A/E should get further from the neutral-atom ratio. As successive ionization potentials increase, the formula will eventually break down, but it is the relative size of the net charge to Z that matters. In our expansion of W_2 and W_1 in powers of $Z^{-1/3}$, we see that changing Z to $Z + q$ still produces an expansion with leading term going as $Z^{7/3}$. Successive electron affinities decrease to zero – the multiply charged negative ions are marginally stable and the addition of an electron essentially does not affect the energy or any of its components. In general, we expect removal of an electron will decrease $|I|$ relative to $|A|$, so $-I/E$ will decrease from its neutral ion value. For negative ions the reverse is true.

In Table 1, we have given the energies and the ratios $-I/E$ for a series of atoms and ions calculated by Czyzak [10]. The numbers used were from the papers of Czyzak [10] and Clementi [11]. For the neutrals $-I/E$ is ~ 0.38 (2/5 or 1/3 predicted from $Z^{12/5}$ or $Z^{7/3}$); for singly positive ions, $-I/E \sim 0.37$, and $-I/E$ decreases with increasing charge; for negative ions, $-I/E$ is about 0.4.

Table 1. *Energy quantities for atoms and ions*

System	$-E$(a.u.)	T(a.u.)	I(a.u.)	$-I/E$
P(^4S)	340.7	340.7	131.3	0.385
P$^+$(^3P)	340.3	340.3	125.1	0.368
P^{++}(^2P)	339.6	339.6	119.2	0.351
P^{+++}(^1S)	338.6	338.6	113.5	0.335
S$^=$	397.5	397.5	166.3	0.418
S$^-$	397.5	397.5	158.9	0.400
S	397.5	397.5	151.6	0.382
S$^+$	397.2	397.2	144.5	0.363
S^{++}	396.3	396.3	136.4	0.346
S^{+++}	395.1	395.1	130.1	0.329
S^{+4}	393.4	393.4	123.6	0.314
Cl$^-$	459.6	459.6	181.6	0.395
Cl	459.5	459.5	175.1	0.381
Cl$^+$	459.0	459.0	167.4	0.365
Cl^{++}	458.2	458.2	157.1	0.343
Cl^{+++}	456.8	456.8	148.6	0.325
Cl^{+4}	454.9	454.9	139.7	0.307
Cl^{+5}	452.4	452.4	132.1	0.292
A	526.8	526.8	201.4	0.382
A$^+$	526.3	526.3	193.6	0.368
A^{++}	525.3	525.3	184.1	0.350
A^{+++}	523.9	523.9	174.3	0.333
A^{+4}	521.7	521.7	164.5	0.315
A^{+5}	519.0	519.0	155.0	0.299
A^{+6}	515.7	515.7	144.2	0.279

Like ionization potentials, binding energies of diatomic molecules are small compared to total energies. The binding energy (BE) is the difference between the internuclear repulsion V_{nn} and the change in the electronic energy $(=A+T+I)$ on bonding. At the equilibrium nuclear configuration, the virial theorem holds [12]. Writing subscripts m for the molecule and 1 and 2 for the atoms to which it dissociates, we have $A_1+I_1=2E_1$, $A_2+I_2=2E_2$, and $A_m+I_m+V_{nn}=2E_m$, with $V_{nn}=Z_1Z_2/R$. Using the Hellmann-Feynman Theorem,

$$A_m=Z_1\partial(E_m-V_{nn})/\partial Z_1+Z_2\partial(E_m-V_{nn})/\partial Z_2\,, \qquad (13)$$

where here and in what follows all partial differentiations are performed with the number of electrons constant. Now $E_m=E_1+E_2-BE$ (taking BE to be positive), and $\partial E_1/\partial Z_2=\partial E_2/\partial Z_1=0$, while $\partial(BE)/\partial Z_i$ is very small, as we have recently discussed [13]. Then (13) yields

$$A_m\approx-2V_{nn}+A_1+A_2\,,$$

where we have used (3). If $A=kE$ for atoms (k is between 7/3 and 12/5), we now have

$$2E_m-I_m-V_{nn}\approx-2V_{nn}+k(E_1+E_2)$$

and neglecting the term BE/E_m,

$$I_m-V_{nn}\approx(2-k)\,E_m \qquad (14)$$

Eq. (14) makes the ratio of I_m-V_{nn} to E_m the same as the ratio of I to E for atoms, about 0.38. One way of expressing this is to say that the internuclear repulsion energy is closely equal to the change in interelectronic repulsion energy on molecule formation.

We give several examples of the validity of (14) in Table 2. BeO and N_2 present no surprises, but we note that the rule holds for HF, in spite of the fact that $A=2E$ for the H atom. This is because the energy of H will be small compared to the energy of the other atom for hydrogen-containing molecules. For a polyatomic such as NH_4Cl, Eq. (14) is valid provided that the atomization energy is small compared to the total energy. Because $A\cong kE$ for atomic ions, the fact that a

Table 2. *Energy quantities for sundry molecules*

Molecule and configuration	Total energy E_m in a.u.	Interelectronic repulsion I	Internuclear repulsion V_{nn}	$\dfrac{I_m-V_{nn}}{E_m}$	Ref.
BeO, $R=2.438\,a_0$	$-\ 89.448$	47.431	13.127	0.384	a
$N_2, R=2.0132\,a_0$	-108.996	62.041	24.339	0.346	b
HF, $R=1.7330\,a_0$	-100.258	45.094	5.193	0.398	c
NH_4Cl, case D-5	-515.831	248.117	51.297	0.382	d
$N_2^+, R=2.0385\,a_0$	-108.408	56.376	24.037	0.298	b
$SH^-, R=2.551\,a_0$	-398.146	163.668	6.272	0.395	e

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molecule dissociates into ions should not change the ratio $(I_m - V_{nn})/E_m$ much. The result for N_2^+ is a little surprising: it may indicate that $\partial(\mathrm{BE})/\partial Z_i$ is not small for ions. Good calculations are not available for heavier molecules, but (14) is expected to hold more exactly for these.

It is hoped that the considerations discussed above may be of some use in explaining the regularities in the partitioning of the energy in atoms and molecules. We have also derived the asymptotic form of the Z-dependence of the energy of neutral atoms [14] as $Z^{7/3}$, and have estimated the coefficient of this term, giving a formula for the energy that is apparently approximately valid, even for Z below 10, which is quite unexpected. From the formula $E = kZ^{7/3}$, the results on the partitioning of the energy follow, as we have indicated.

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