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The Principle of Maximum Hardness

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Density functional theory (DFT) is a branch of quantum mechanics in which the emphasis is on the one-electron density function, ρ, rather than on the more usual wave function.[1] It goes back to the work of Hohenberg and Kohn, who proved that the ground-state energy of a chemical system is a functional of ρ only. A chemical system is a collection of nuclei and electrons. It may be an atom, an ion, a radical, a molecule, or several molecules, in a state of interaction. A functional is a recipe for turning a function into a number, just as a function is a recipe for turning a variable into a number.

There are many important applications of DFT to chemistry. One is in the calculation of properties of atoms and molecules. These are much easier than and of similar accuracy to calculations using very good wave functions. For a system containing N electrons, the wave function depends on $4N$ space and spin coordinates. The electron density depends on only three space coordinates, and N enters as a simple multiplicative factor. Hence computations are very much simpler in DFT, especially for large systems.

Another important use for DFT is in elucidating familiar chemical concepts. Since 1975, R. G. Parr and his co-workers have been particularly active in this area. The present paper will deal with two new properties of a chemical system, arising from this work. They are the electronic chemical potential, μ,[2] and the hardness, η.[3] These are of great importance in determining the behavior of the system, and they lead to broadly applicable and useful principles.

The definitions of these quantities are

$$\mu = (\partial E/\partial N)_\nu; \qquad 2\eta = (\partial \mu/\partial N)_\nu = 2/\sigma \qquad (1)$$

where E is the energy, N is the number of electrons, and ν the potential due to the fixed nuclei. The softness, $\sigma = 1/\eta$, is also a useful quantity. The name electronic chemical potential comes from the thermodynamic equation

$$\mu_0 = (\partial E/\partial N)_{S,V} \qquad (2)$$

Here μ_0 is the ordinary chemical potential, and N is the number of molecules. The two, μ and μ_0, are alike in that, at equilibrium, they must be constant everywhere in the system.

Classical thermodynamics also gives us

$$(\partial \mu/\partial N)_{V,T} = -V^2(\partial P/\partial V)/N^2 = V/N^2\kappa \qquad (3)$$

where κ is the compressibility and N is again the number of molecules. Comparison with eq 1 shows that the chemical softness, σ, is analogous to the mechanical softness, κ.

In spite of these similarities, there is no real relationship between the two sets of quantities. The electronic chemical potential is *not* the electronic part of the thermodynamic chemical potential. The chemical hardness is not resistance to mechanical deformation, but resistance to change in the number of electrons in the system, or to changes in the one-electron density function, ρ.

Operational, and approximate, definitions of μ and η are

$$-\mu = (I + A)/2 = \chi; \qquad \eta = (I - A)/2 \qquad (4)$$

where I is the ionization potential and A is the electron affinity of the system. χ is the absolute electronegativity. It is similar to, but not equal, to the Mulliken electronegativity.

If we draw a plot of E vs N for any system, then μ is simply the instantaneous slope of such a curve. Experimentally we only know points on the curve for integral values of N, from data such as ionization potentials and electron affinities. We do not know the instantaneous slope of the curve. However, if we pick the neutral species (or any other) as our starting point, we do know the mean slope for the change from $(N - 1)$ to N electrons. It is simply equal to $-I$. Also the mean slope from N to $(N + 1)$ electrons is simply $-A$. Using the method of finite differences, we can approximate the slope at N as $-(I + A)/2$.

In the same way, 2η is the curvature of a plot of E vs N. Using finite differences again gives $\eta = (I - A)/2$. The factor of 2 was added arbitrarily to make μ and η symmetrical.

According to Koopmans's theorem, the ionization potential is simply the orbital energy of the HOMO, with change in sign. For spin-paired molecules, the electron affinity is the negative of the orbital energy of the LUMO; therefore, on an orbital basis, we can write

$$\mu = (\epsilon_{\mathrm{HOMO}} + \epsilon_{\mathrm{LUMO}})/2; \qquad \eta = (\epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}})/2 \qquad (5)$$

If we make the usual diagram of the MOs of a molecule as a function of their energies, μ is a vertical line halfway between the HOMO and the LUMO. The hardness is just half the energy gap between the two.[4]

Thus a hard molecule has a large energy gap, and a soft molecule has a small gap. In MO theory, the frontier orbitals also define the lowest excited state of

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(1) For a general introduction, see: Parr, R. G.; Yang, W. *Density Functional Theory for Atoms and Molecules*; Oxford Press: New York, 1989.

(2) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* 1978, *68*, 3801–3807.

(3) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512–7516.

(4) Pearson, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 8440–8441.

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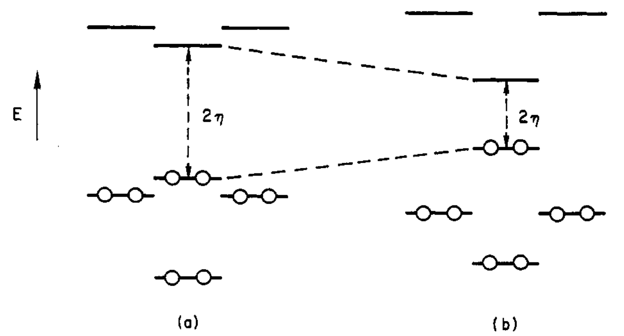

Figure 1. Orbital energies for NH_3: (a) pyramidal form; (b) planar form.

the molecule. A large energy gap means a large energy difference between the ground state and the manifold of excited states of the same multiplicity.

This is of great importance, since the quantum mechanical theory of response to a perturbation in a chemical system depends on this difference.[5] Changes in electron density occur by mixing excited-state wave functions with the ground-state wave function. The mixing coefficient is inversely proportional to the energy difference between the states. Therefore soft molecules undergo changes in electron density, ρ, more readily than hard molecules.

Circumstantial Evidence Concerning Hardness

The foregoing suggests that it is a good thing for a chemical system if it can arrange itself to be as hard as possible.[6] Since chemical reactions obviously require changes in the electron density distribution pattern, we expect soft molecules to be more reactive than hard molecules, in general. This is indeed the case.[4,7] For example, H_2S, with $\eta = 6.2$ eV, is certainly more reactive and less stable than H_2O, with $\eta = 9.5$ eV. H_2Se and H_2Te are softer and more reactive still.

A classic example is provided by the benzenoid hydrocarbons.[8] A plot of the experimental values of $I - A$ against the resonance energy per electron (REPE) is a straight line. The REPE is a good measure of aromatic character, that is, reactivity and stability. Benzene has the largest value of $I - A$ and is the most stable and least reactive. Pentacene has the smallest value of $I - A$ and is the most reactive.

Theoreticians who do MO calculations of molecular structures and energies always seem to find that the most stable structure has the largest HOMO-LUMO energy gap.[6,9] Figure 1 illustrates this by showing an MO energy diagram for NH_3 in its stable pyramidal form, and in the unstable planar form.

The smaller gap in the latter case arises because the p_z orbital of nitrogen is removed from bonding while still occupied. Thus it becomes the HOMO. A linear combination of hydrogen 1s orbitals is removed from an antibonding MO, is lowered in energy, and becomes the LUMO.

Table I shows the results of some calculations by the extended Huckel method for the *closo*-borane anions.[10]

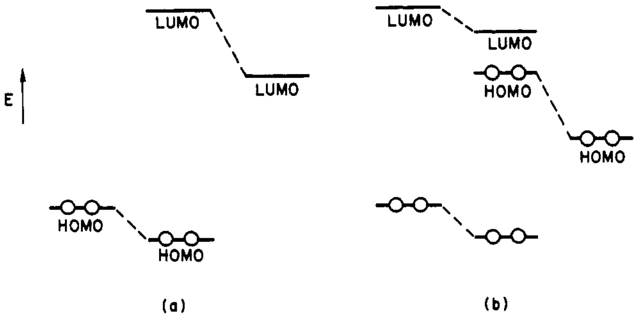

Figure 2. Energy changes during the approach of two subsystems: (a) HOMO-LUMO interaction; (b) HOMO-second filled orbital interaction.

Table I. Results of Molecular Orbital Calculations for the *closo*-Boranes[a]

borane anion	idealized geometry	ΔE gap, eV	borane anion	idealized geometry	ΔE gap, eV
$B_6H_6^{2-}$	O_h	6.6	$B_7H_7^{2-}$	C_{3v}	0
$B_6H_6^{2-}$	D_{3h}	1.1	$B_8H_8^{2-}$	D_{2d}	2.5
$B_7H_7^{2-}$	D_{5h}	5.9	$B_8H_8^{2-}$	D_{4d}	3.2
$B_7H_7^{2-}$	C_{2v}	1.2	$B_8H_8^{2-}$	C_{2v}	2.2

[a] From ref 10.

The HOMO-LUMO gap is given for $B_6H_6^{2-}$ and $B_7H_7^{2-}$, for both the stable structure and unstable ones. In both cases the energy gap is much larger for the stable structure. For $B_8H_8^{2-}$ the gap is calculated for three possible structures. No strong preference for any of these is found. In agreement with this, the ion has been found to be fluxional.

An examination of orbital interactions when two partial systems approach each other can be informative. Assume that the HOMO and the LUMO play the dominant role in these interactions. Figure 2a shows the interaction of the frontier orbitals. The lower energy orbital, the HOMO, goes down in energy, and the LUMO goes up. There is a net energy lowering, and the gap increases. Figure 2b shows the case where the HOMO is interacting mainly with another filled orbital. Now the HOMO goes up in energy. The LUMO will mix primarily with other empty orbitals, which will lower its energy, as shown. The net effect is that the energy is raised and the HOMO-LUMO gap is diminished.

This is the result for orbital interactions, or covalent bonding. What about ionic bonding? Consider an anion and a cation approaching each other, with a net decrease in energy. The HOMO will be an atomic orbital on the anion, and the LUMO will be an orbital of the cation, in the usual case. As the ions approach, the potential of the cation will lower the orbital energy of the HOMO, and the potential of the anion will raise the orbital energy of the LUMO. The HOMO and LUMO will move apart, just as in Figure 2a.

Thus covalent and ionic bonding give similar results. However, it must be remembered that these remarks apply only to the orbital energies. The total energy must also include the nuclear-nuclear repulsion.

The preceding examples refer to hardness as a function of nuclear positions. Equally important is the relationship of hardness to the electron density function, ρ. Will the hardness increase to a maximum value as

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(5) This is often discussed under the heading of the second-order Jahn-Teller effect. See: Pearson, R. G. *Symmetry Rules for Chemical Reactions*; Wiley-Interscience: New York, 1976.

(6) Pearson, R. G. *J. Chem. Educ.* **1987**, *64*, 561-567.

(7) Pearson, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 2092-2097.

(8) Zhou, Z.; Parr, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 7371-7379.

(9) (a) Bartell, L. S. *J. Chem. Educ.* **1968**, *45*, 754-758. (b) Burdett, J. K.; Coddens, B. K.; Kulkarni, G. V. *Inorg. Chem.* **1988**, *27*, 3259-3261.

(10) Muetterties, E. L.; Beier, B. F. *Bull. Soc. Chim. Belg.* **1979**, *84*, 397-401.

(11) See: Zhou, Z.; Parr, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 5720-5724.

a set of trial wave functions becomes progressively better, approaching the true wave function?

Some conclusions can be drawn, if we restrict ourselves to LCAO-MO theory. The eigenfunctions, ϕ_m, are given by

$$\phi_m = \sum C_{ml}\psi_l \tag{6}$$

where the ψ's are atomic orbitals. The orbital energies are found from the determinant

$$|H_{ij} - S_{ij}\epsilon| = 0 \tag{7}$$

The conditions for the solutions are that

$$(\partial\epsilon_m/\partial C_{ml}) = 0; \quad (\partial E/\partial C_{ml}) = 0 \tag{8}$$

All the roots are maxima or minima on the energy-coefficient hypersurface. The lowest root is the absolute minimum, the highest root is the absolute maximum, and the remaining roots are local maxima and minima. The occupied orbitals, in virtually all cases, will have negative curvatures, $(\partial^2\epsilon/\partial C_{ml}^2)$, corresponding to bonding MOs, or zero curvature, nonbonding orbitals. The empty orbitals will have positive curvatures, antibonding, or zero curvature. This applies to the HOMO and LUMO, in particular.

The best values of the C_{ml}'s define the best wave function, and the best value of ρ, that can be obtained from the selected basis set of AOs. Any change from the best values will cause the HOMO to rise in energy, or be unchanged, and the LUMO will fall in energy, or be unchanged. Thus the energy gap between them is a maximum for the best values of the coefficients, or the "best" electron density function. Usually, of course, this will not be the true density function.

The conclusion that the hardness has a maximum value for the lowest energy solution can be readily verified in simple cases, such as the Huckel MO theory. Inclusion or omission of overlap integrals has no effect. Examples where all atoms are the same and cases where the atoms and the orbitals are different give the same result.

Provided the SCF condition is met, calculations at the Hartree–Fock level also obey the mathematics of eqs 4 and 5. Therefore the HOMO–LUMO gap should also be a maximum in these cases. Because the solutions are normalized and orthogonal, and because the atomic orbitals are conserved, the coefficients for different MOs are not independent. Therefore wrong coefficients in one orbital will usually lead to wrong coefficients in all orbitals.

We can also change the trial wave function for a system by enlarging the basis set of atomic orbitals. If this is done, what usually happens is that the HOMO is changed only slightly, usually to a more negative energy. But the LUMO is decreased in energy much more, so that the HOMO–LUMO gap is smaller, even though the total energy is decreased. At the same time, the value of μ becomes more negative, because of the decrease in ϵ_{LUMO}. This turns out to be important, as will be seen in the next section.

The Principle of Maximum Hardness

The evidence of the previous section is suggestive of some principle of maximum hardness (PMH). But none of it is rigorous enough or general enough to be conclusive. Fortunately Parr and Chattaraj have recently given a rigorous and general proof, using a combination of statistical mechanics and density functional theory.[12]

One starts with a grand canonical ensemble of identical systems in equilibrium at temperature T and electronic chemical potential μ. The softness, σ, can then be defined in terms of fluctuations in N from the average value $\bar{N}$.[13]

$$\sigma = (\partial N/\partial\mu)_\nu = \beta\langle(N - \bar{N})^2\rangle \tag{9}$$

where $\beta = 1/kT$, as usual. Soft systems have large fluctuations.

The softness, which is an average value, can also be written as

$$\sigma = \beta\sum P^{\circ}_{N,i}(N - \bar{N})^2 \tag{10}$$

where the $P^{\circ}_{N,i}$ are the equilibrium probabilities.

$$P^{\circ}_{N,i} = (F)^{-1}\exp[-\beta(E_{N,i} - N\mu)] \tag{11}$$

F is the grand partition function.

A nonequilibrium ensemble would be characterized by a set of probabilities, $P_{N,i}$, different from the equilibrium values. We can write

$$\sigma' = \beta\sum_{N,i} P_{N,i}(N - \bar{N})^2 \tag{12}$$

Now the fluctuation–dissipation theorem of statistical mechanics[14] may be used to show that $\sigma' - \sigma > 0$. Thus the equilibrium state has the minimum softness, or maximum hardness, of all the possible states.

The proof depends on μ, ν, and T being constant. The potential μ appears in eq 11 because it is also the Lagrange multiplier for the normalization constraint. While the details are not simple, they are standard statistical mechanics. N is the number of electrons, not the number of molecules, as is more usual.

The requirement that μ and ν remain constant is very restrictive. However, there are examples where it can be met. The potential of the nuclei, ν, is constant if the geometry is fixed. For two-orbital, two-electron cases, the HOMO and the LUMO approach each other symmetrically, when overlap is ignored. Their midpoint, which is μ, is unchanged. Alternant hydrocarbons behave in the same way.

This agrees with the observations of the previous section, that the HOMO–LUMO gap is a maximum for the best values of the C_{ml} coefficients. In other cases, while μ is not constant, its change may be very small. To what extent this is true for Hartree–Fock calculations is a question still to be examined.

Fortunately, there are also ways to examine the principle of maximum hardness, even for changes in the nuclear positions.[15] Start with a molecule in its equilibrium geometry and calculate the orbital energies at, or near, the HF level. Now distort the molecule a small distance along directions given by the vibrational symmetry coordinates, and recalculate the orbital energies. By using the complete set of symmetry

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(12) Parr, R. G.; Chattaraj, P. K. *J. Am. Chem. Soc.* **1991**, *113*, 1854–1856.

(13) Yang, W.; Parr, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 6723–6726.

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(15) Pearson, R. G.; Palke, W. E. *J. Phys. Chem.* **1992**, *96*, 3283–3285.

Table II. Distortions of Carbon Dioxide from the Equilibrium Geometry

R_1	R_2	θ	$-\epsilon_{\mathrm{HOMO}}$	ϵ_{LUMO}	$-2\mu^b$	$2\eta^b$
1.1352	1.1352[a]	180° [a]	0.5423	0.2307	0.3116	0.7730
1.1052	1.1652	180°	0.5405	0.2313	0.3092	0.7718
1.1652	1.1052	180°	0.5405	0.2313	0.3092	0.7718
1.1052	1.1052	180°	0.5438	0.2391	0.3047	0.7829
1.1652	1.1652	180°	0.5407	0.2066	0.3341	0.7473
1.1352	1.1352	175°	0.5419	0.2098	0.3321	0.7517
1.1352	1.1352	185°	0.5419	1.2098	0.3321	0.7517

[a] Equilibrium values. From ref 16. [b] In atomic units.

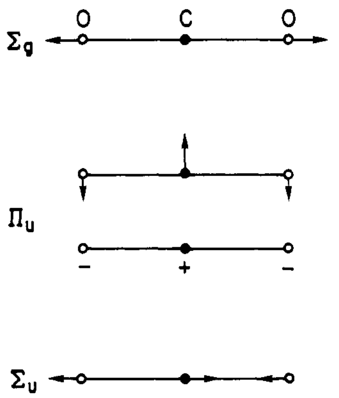

Figure 3. Vibrational modes of CO_2 in $D_{\infty h}$ point group.

coordinates, the hardness can be probed for all possible changes in the equilibrium geometry.

Table II shows the results of such calculations for the CO_2 molecule.[16] In order to understand the results, Figure 3 shows the normal modes of vibration of CO_2. The asymmetric modes, Π_u and Σ_u, differ from the symmetric mode, Σ_g, in several respects. First of all, they destroy some elements of symmetry, changing the point group to C_{2v} and $C_{\infty v}$, respectively.

Secondly, positive deviations from equilibrium produce a configuration which gives the same average nuclear potential as negative deviations. Therefore, ϵ_{HOMO}, ϵ_{LUMO}, μ, and η must be the same for both. If we let Q represent a symmetry coordinate, then both $(\partial\mu/\partial Q)$ and $(\partial\eta/\partial Q)$ must be equal to 0 at the equilibrium Q_0.

Also, if we expand the energy as a power series in ΔQ, the linear term must vanish, and the quadratic term is the first nonvanishing one. Symmetry arguments can be used to show that $(\partial v_n/\partial Q)$ and $(\partial v_e/\partial Q)$ are separately equal to 0 when averaged.[17] Here v_n and v_e refer to the potentials of the nuclear repulsion and the nuclear–electron attraction, respectively.

Hence, for the non-totally symmetric distortions, we have met the restrictions of Parr and Chattaraj. Accordingly, the hardness should be a maximum at Q_0. Table I shows that this is the case. Note that μ can either decrease or increase upon distortion from equilibrium.

The totally symmetric mode gives different results. The hardness and μ both increase steadily as the nuclei approach each other. If the nuclei coalesced, μ would be a maximum. This does not happen because at Q_0 we have the condition

$$\langle(\partial v_e/\partial Q) + (\partial v_n/\partial Q)\rangle = 0 \qquad (13)$$

Thus the equilibrium value of Q is determined by the Hellman–Feynman theorem of balanced forces, and not by the maximum value of μ. This is not a violation of the PMH since neither ν nor μ remains constant.

Table III. Changes in η for Bond-Forming Reactions

reaction	η_R,[a] eV	η_P,[b] eV
$Na + Cl = NaCl$	0.8	4.8
$Li + F = LiF$	1.0	5.4
$Li + H = LiH$	2.3	3.8
$H + Cl = HCl$	4.7	8.0
$C + O = CO$	4.9	7.9
$H + OH = H_2O$	5.7	9.5
$CH_3 + F = CH_3F$	3.2	9.4
$CH_3 + Cl = CH_3Cl$	3.1	7.5
$CH_3 + Br = CH_3Br$	3.2	5.8
$CH_3 + I = CH_3I$	3.4	4.7
$Ni + CO = NiCO$	3.3	3.6
$Cr + 6CO = Cr(CO)_6$	3.1	4.5
$Fe + 2C_5H_5 = Fe(C_5H_5)_2$	2.8	3.8
$Cr + 2C_6H_6 = Cr(C_6H_6)_2$	3.1	3.3

[a] Hardness of reactants. [b] Hardness of products. From ref 18.

These results for CO_2 are typical. The same features have been found for H_2O,[16] NH_3,[15] and C_2H_6.[15] The latter molecule is a good test, since there are three symmetric modes and nine asymmetric ones. While the equilibrium distances and angles in a molecule are determined by eq 13, the existence of symmetry in a molecule is determined by the hardness.

If the hardness decreases upon any distortion that destroys an element of symmetry, that element is stable. If η increases, the molecule will spontaneously distort and the element will vanish. An example would be NH_3 in a planar form.[15] These results are strikingly similar to those deduced from the second-order Jahn–Teller effect.[5]

Other Observations

There are still further reasons to believe that increasing hardness accompanies the approach of a chemical system to equilibrium. Consider the overall process

$$N(g) + 3H(g) = NH_3(g) \qquad (14)$$

which is very favorable energetically. We can calculate the overall changes in μ and in η, using experimental values of I and A and eq 4. We find that μ increases from −7.2 to −2.6 eV, and η increases from 6.4 to 8.2 eV.

Examination of a large number of reactions where a few atoms or radicals form a molecule always shows that the hardness increases.[18] The electronic chemical potential may increase or decrease. Table III gives a number of examples of the changes in η.[19]

These results are consistent with Figure 1. As long as the energy is decreasing, the HOMO–LUMO gap is

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(16) Palke, W. E. Unpublished calculations.

(17) Pearson, R. G. *Acc. Chem. Res.* **1971**, *4*, 152–160.

(18) Pearson, R. G. *Inorg. Chim. Acta* **1992**, *198–200*, 781–786.

(19) To find I and A for a mixed system, take the smallest I and the most positive value of A. Perdew, J. P.; Parr, R. G.; Balduz, J. L. *Phys. Rev. Lett.* **1982**, *49*, 1691–1694.

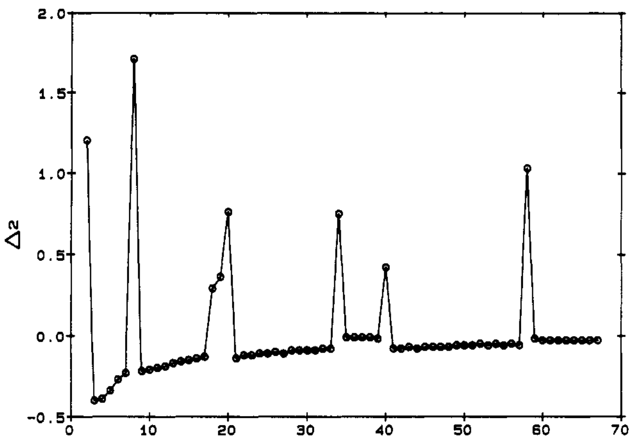

Figure 4. Second energy differences, Δ_2, for lithium clusters versus the number of atoms, N. Reprinted with permission from ref 21. Copyright 1992 National Academy of Sciences.

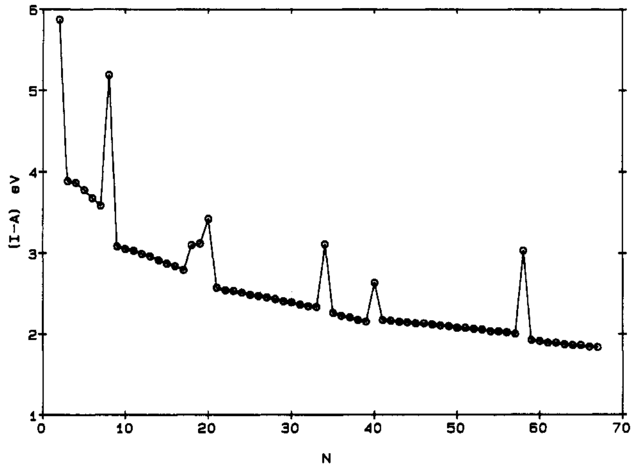

Figure 5. Chemical hardness, $I-A$, versus the number of atoms, N, for lithium clusters. Reprinted with permission from ref 21. Copyright 1992 National Academy of Sciences.

increasing. A maximum in η is not reached when the total energy is a minimum, because Figure 1 does not include the nuclear repulsion term. The PMH is not violated because ν and μ are not constant.

The mass spectra of clusters, both metallic and nonmetallic, show enhanced intensity for certain numbers of atoms, called magic numbers. For clusters of alkali metal atoms, the magic numbers are N = 2, 8, (18), 20, 34, 40, and 58.[20] Figures 4 and 5 show the results of some theoretical calculations on lithium clusters using the spherical jellium background model.[21]

The cluster stability is shown by plotting the second energy difference.

$$\Delta_2 = E(N+1) - E(N-1) - 2E(N) \qquad (15)$$

Figure 4 shows that Δ_2 is close to 0, except for N = 2, 8, 18, 20, 30, 40, and 58. The peaks at these numbers show that the model is working well.

Figure 5 shows a plot of η as a function of N, using eqs 4 and 5. There is a general decrease of $(I - A)$ as N increases. However, there are pronounced peaks again at N = 2, 8, 18, 20, 34, 40, and 58. At the magic numbers the hardness shows a local maximum. Increased stability is accompanied by increasing hardness.

As N becomes very large, we approach metallic lithium. I becomes equal to A, and both are equal to the work function for the metal. The reason for this, of course, is the band structure of the solid. In a metal, the valence band is only partly filled, so the highest occupied level has virtually the same energy as the lowest empty one.

The process

$$\mathrm{Li(g)} = \mathrm{Li(s)} \qquad (16)$$

is downhill in energy, but the hardness *decreases* from 2.4 to 0.0 eV. The potential μ remains surprisingly constant, being −3.0 eV for lithium atoms and −3.1 eV for lithium metal.[22] Since the nuclear potential changes greatly in eq 16, there is no violation of the PMH.

For insulating solids and semiconductors there is also an overall decrease in η in going from the gas phase to the solid.[19] However, just as for single molecules, the space group symmetry of solids appears to be determined by the energy gap. The most stable structure is the one with the largest gap.[9]

Just as for the aromatic hydrocarbons, the stability of the fullerenes, C_n, depends on the HOMO–LUMO gap.[23] In addition, there is a geometric factor in that there must be the right number of carbon atoms to form a suitable cage. Calculations, using density functional theory, show that C_{32}, C_{60}, C_{70}, C_{90}, and C_{100} have a large gap and should be stable; but C_{12} and C_{24} have a zero gap and should not exist.

Concluding Remarks

The examples of the preceding reactions are all consistent with the statement that "at equilibrium, chemical systems are as hard as possible". The hardness is a maximum for changes that do not also change μ or ν, as predicted by Parr and Chattaraj. Some relaxation of these restrictions seems to be allowable, and it is possible that a more general, and less restrictive, rule may be found.

A potential use for the PMH is in finding the best approximate wave function for a chemical system. Since changing the basis set usually changes μ as well as η, this is a case where the more general rule is needed. In the case of isomers where a difference in the bonding between atoms occurs, the PMH does *not* predict that the most stable isomer has the largest HOMO–LUMO gap. Such isomers will necessarily have quite different values of ν, though μ can be fairly constant. An examination of a number of isomers show that the nuclear–nuclear repulsions most often dominate the relative stabilities.

Usually each isomer has a local energy minimum in the energy-nuclear position hypersurface. The same rules as outlined for CO_2, NH_3, C_2H_6, and H_{20} will apply to each isomer. The hardness should be a maximum with respect to antisymmetric distortions from the geometry of the local energy minimum.

The factors that change the hardness are fairly well understood, though a calculation from first principles

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[20] de Heer, W. A.; Knight, W. D.; Chou, M. Y.; Cohen, M. L. *Solid State Physics* **1987**, *40*, 93–181.

[21] Harbola, M. K. *Proc. Natl. Acad. Sci. U.S.A.* **1992**, *89*, 1036–1039.

[22] The values of μ are remarkably similar for all metal atoms and their solid metal forms. Pearson, R. G. *Chem. Br.* **1991**, 444–447.

[23] Kurita, M.; Kobayoshi, K.; Kumahora, H.; Tago, K.; Ozawa, K. *Chem. Phys. Lett.* **1991**, *188*, 181–185.

is not straightforward.[24] The factors are the changes in the kinetic energy and the interelectronic repulsion as ρ is changed. Changes in ρ are due to changes in N, or to changes in the shape factor of ρ at constant N.

When a subshell is being filled, the changes in interelectronic repulsion are dominant. When a shell is filled, there is a big change in kinetic energy for the next electron added. This causes a large change in η.[25] There are a number of important consequences of this. These will be discussed in the following Account in this issue, by Zhou and Parr.

A corollary of the PMH has to do with the properties of the transition state. Long ago Bader pointed out that an activated complex must have very low lying excited states.[26] We can now speculate that it must have a minimum energy gap between the HOMO and the LUMO. Certainly this should be so for a reaction coordinate (for decomposition) that is not totally symmetric. There is some evidence that the gap is a minimum, even when the transition state is of low symmetry.[27]

It appears that the PMH is a fundamental, broadly applicable electronic-structure rule. In this it resembles the other general rule derived from density functional theory: the electronic chemical potential must be constant everywhere in a chemical system at equilibrium![2] This is the famous "electronegativity equalization" rule, if eq 4 is used to define the electronegativity.

To appreciate the broad applicability of the PMH, one need only look at the proof as given by eqs 9–12. These use only the laws of probability applied to large systems. Yet the conclusion can be applied at once to properties of the frontier orbitals of single molecules. It is noteworthy that this application seems to work so well, even though eq 5 is a fairly severe approximation. Also all levels of MO theory seem to be covered equally well.

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(27) Datta, D. *J. Phys. Chem.* **1992**, *96*, 2409–2410.