Absolute Hardness: Unifying Concept for Identifying Shells and Subshells in Nuclei, Atoms, Molecules, and Metallic Clusters

ROBERT G. PARR* AND ZHONGXIANG ZHOU

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290

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Shells and subshells, and the singular importance of closed shells, are ideas that permeate the theory of the structure of matter at all levels, from atomic nuclei, to atoms and molecules, to metallic clusters. In this Account we argue that the absolute hardness is generally a most useful quantitative index for marking the closing of shells, and we point out that the closing of shells can be described as a consequence of the principle of maximum hardness. The preceding Account reviews evolution of the maximum hardness principle.[1]

The atomic nucleus is especially stable when the number of protons or neutrons equals 2, 8, 20, 28, 50, 82, or 126, the "magic numbers" in nuclear physics.[2] These stable nuclei are more abundant in nature than their neighbors, and many nuclear properties show peculiarities at these magic numbers. For atoms, the shell structure was known even before the advent of quantum mechanics. The periodic table itself is nothing but a concise summary of experimental observations of atomic shell structures. Closed shell atoms are chemically stable by themselves while open shell atoms are only found in molecules. The changes in chemical and physical properties of atoms across a period in the periodic table are not smooth. Subshell effects are evident though they are not as pronounced as main shell effects. Shell structure in metallic clusters has been studied only recently.[3,4] The experimental mass spectra of small alkali-metal clusters show that the clusters are more stable at the "magic" atomic numbers 8, 20, 40, 58, 92, ... Some fine structure in the mass spectra suggests the existence of subshells in these clusters.[4]

Theoretically the shell structures are obtained quite differently for different levels of matter. At the nuclear level a model Hamiltonian with a central potential plus a spin-orbit coupling interaction potential produces a good prediction of the magic numbers though the actual nuclear structure is much more complicated than this simple model would appear to imply.[1] The spin-orbit coupling term in the potential is crucial for the correct prediction of the magic numbers. At the atomic level, a central field Hartree-Fock approximation is sufficient to generate the shell structure, including the subshells. Most trends across the periodic table can be explained in this approximation. For metallic clusters the spherical jellium background model (SJBM) provides a reasonable explanation of the shell structure.[3-8] Though the theoretical models used in predicting the shell structures in nuclei, atoms, molecules, and metallic clusters are quite different, the quantities used conventionally in locating the shells are similar: either the energy per particle or the second difference, $\Delta_2 E = E(N_A+1) + E(N_A-1) - 2E(N_A)$, where N_A is the number of particles. Note that the "pair potential" defined by Burdett and Fässler[9] is the negative of just such a $\Delta_2 E$ with N_A the number of ligands in a molecular cluster.

Absolute hardness η is defined as one-half of the second derivative of energy E with respect to the number of particles N:[10]

$$\eta = {}^1/_2 \left[\frac{\partial^2 E}{\partial N^2}\right]_{v(\vec{r})} \qquad (1)$$

where $v(\vec{r})$ is the external potential (here kept fixed). The finite difference approximation to eq 1 is

$$\eta = (I - A)/2 \qquad (2)$$

where I is the ionization potential and A the particle affinity. If an orbital theory is used, η becomes[11]

$$\eta = (\epsilon_L - \epsilon_H)/2 \qquad (3)$$

where ϵ_H is the energy of the highest occupied molecular orbital (HOMO) and ϵ_L is the energy of the lowest unoccupied molecular orbital (LUMO). For solids η is half the band gap. For metals $\eta = 1/2g(\epsilon_F)$, where $g(\epsilon_F)$ is the total density of states at the Fermi energy ϵ_F.[12] Softness is the inverse of hardness.[12]

Usually, but not always, the particles are electrons. The sensitivity function $\Delta_2 E$ is a hardness in the sense

Born in Chicago, IL, in 1921, Robert G. Parr received the A.B. from Brown University in 1942 and the Ph.D. from the University of Minnesota in 1947. Presently he is Wassily Hoeffding Professor of Chemical Physics at the University of North Carolina at Chapel Hill, NC. He has done research for many years on the quantum theory of the electronic structure of molecules, with the density functional theory the most recent emphasis.

Zhongxiang Zhou, born in Hubei, China, in 1959, attended Jilin University (B.S., 1982; M.S., 1985). He received the Ph.D. from the University of North Carolina at Chapel Hill in 1990 and now is Research Associate there. His research interests include conceptual density functional theory, computational density functional theory, molecular orbital graph theory, local methods of solving the Schrödinger equation, and the calculation of electronic properties of large systems.

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that it becomes the hardness of eq 1 when we take the atoms to be the particles involved.

For the purpose of this discussion, eqs 1 and 2 may be regarded as interchangeable. Equation 3 shows that hardness and HOMO–LUMO gap are the same thing.[11]

There is a maximum hardness principle which asserts that systems tend to be as hard as possible.[13] This conclusion was first drawn from experimental facts.[13] Theoretical considerations led to a refined statement of the principle. Under conditions of constant temperature and chemical potential (negative electronegativity), systems tend to a state of maximum hardness.[14,15] Here chemical potential is the average of ϵ_H and ϵ_L or the negative of the average of I and A. A proof within the Hückel molecular orbital (HMO) method goes as follows:[14] For a conjugated organic molecule, the HMO total energy is $E = N\mu + G\beta$ and the HMO hardness is $\eta = A\beta$, where N is the number of carbons in the conjugated system, $G > 0$ and $A < 0$ are external-potential-dependent (or adjacency-matrix-dependent) numbers, μ is the chemical potential, and β is the resonance integral. β is a functional of density, since the effective Hamiltonian which defines β depends on density. If we disturb the equilibrium density in such a way that the chemical potential is unchanged, then the β value will change accordingly, i.e., $|\beta|$ will become smaller. This change makes the total energy less negative and the hardness less positive. This proves the maximum hardness principle within the Hückel theory. A more general proof of the principle has been given that uses statistical mechanics and a fluctuation formula for the softness.[15]

The maximum hardness principle is easily understood from eq 2. Bigger η means larger I and smaller A, which implies that the system has a smaller tendency to accept particles and/or a smaller tendency to give away particles. That is, the system is stable.

With this maximum hardness principle one can easily find the shells in nuclei, atoms, molecules, and metallic clusters. Hardness maxima correspond to closed shells and closed subshells. For nuclei, the particles concerned are nucleons. The corresponding hardness can be chosen as half the difference between the highest filled nuclear energy level and the lowest unfilled one. This difference is bigger for the closed shells, as compared with the neighboring open shells.[16] Shells can be identified by locating the maxima of these energy differences. For atoms, molecules, and metallic clusters, the hardness will take the form familiar to the chemical community; that is, the particles concerned are electrons. The hardness criterion has been very successful in predicting the magic numbers for Li clusters.[8] We expect that it will produce the same results for other metallic clusters, at least in the SJBM description.

Atomic hardnesses are plotted versus atomic number Z in Figure 1. The hardness data are from spin-polarized density functional calculations[17] using the Gunnarsson–Lundqvist exchange-correlation functional.[18] The shell structures are clear in this figure, as are subshell structures. Hardnesses of completely filled s-shells and half-filled p-shells are seen to be local maxima. Exceptions to the subshell feature appear for large Z, possibly caused by the approximation made in the exchange-correlation functional and/or the neglect of relativistic effects. The ionization potential plot analogous to Figure 1 shows shell structure, of course, but it shows subshell structure less well than does Figure 1.

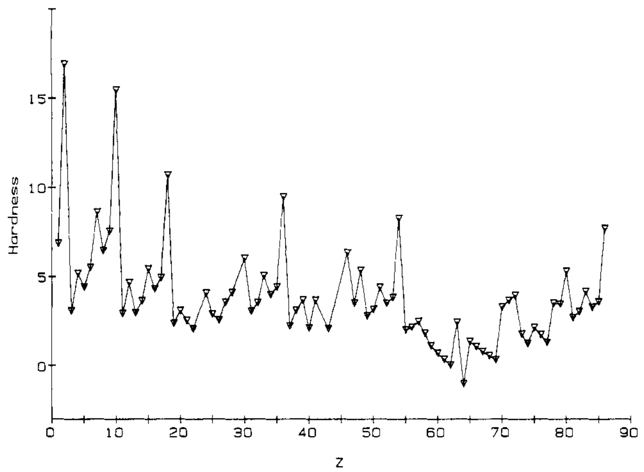

Figure 1. Atomic hardness (in eV) versus atomic number Z. The shells and subshells are determined by the local maxima of hardness.

Figure 1 shows that the maximum hardness principle subsumes the octet principle postulated by Lewis[19] and Langmuir[20] and the 18-electron rule (or the Sidgwick's effective atomic number rule), which is important for transition metals.[21] Molecules of course also show shell structure. An example of this from organic chemistry is the famous Hückel ($4n + 2$) rule. An example from inorganic chemistry could be the Wade–Mingos ($2n + 2$) rule.[22] Or, there is the simple molecular orbital rule that a neutral molecule is thermodynamically stable if all the bonding molecular orbitals are completely occupied and all antibonding orbitals are completely empty.[23] The correspondence between the filling of shells and hardness maxima pervades structural chemistry.

A rough way to understand the reasonableness of using hardness (or equivalently energy gap $\epsilon_L - \epsilon_H$) to locate shells is to examine the energy level distribution of single particles, in a simple independent-particle view of a system. In this description, as we put particles into energy levels from the lowest to the highest, the energy change will deviate from its normal pace when we come to a large energy gap. A system with a particle occupying the level next above the large gap will be less stable than its neighbor with one particle less, which in turn is more stable than the system with one more particle less because of its readily available empty level.

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A big advantage of using hardness as the function that locates shells is that when we use the defining eq 2 for hardness, the quantities concerned are physical observables. Hardness thus can be obtained experimentally, and the definition does not lean on any independent-particle model. Further, note that when eq 3 is used, the computation involves one system only.

By now the hardness concept has been much discussed in the chemistry literature, both qualitatively and quantitatively.[1,8,10–15,24–26] Chemical hardness is well understood to be the resistance of the electronegativity to the change in electron density distribution.[10,27,28] The chemical concept aromaticity, which signifies extra stability of a class of molecules, has been quantified by using the hardness.[29–31] That is to say, the chemical hardness has been established as a measure of the stability of an electronic system. In the chemical literature the HOMO–LUMO gap also has been used widely for some time. For example, the HOMO–LUMO gas has been proposed to be a criterion of stability for ionic crystals.[32,33] Small HOMO–LUMO gaps have been variously connected with instabilities,[34–39] and large gaps with stability.[40–42] For a two-partner electron transfer chemical reaction the hardness of the initial system is half the energy difference between the HOMO of the electron donor and the LUMO of the electron acceptor.[14] The latter is a widely used reactivity index.[43] The smaller this energy difference is, the more reactive the system is. This conforms to the maximum hardness principle. We therefore commend taking hardness as a stability measure in determining the shells and subshells in nuclei, atoms, molecules, and metallic clusters.

There is a companion concept, of comparable importance to the hardness concept, the chemical potential. This is the first derivative of energy with respect to the number of particles.[44] Or, it is the average of ϵ_{HOMO} and ϵ_{LUMO}. Or, it is the Fermi energy. The development of the maximum hardness principle in refs 12 and 13 implies a restriction of constant chemical potential. This restriction probably is important in many cases. For example, both chemical potential and chemical hardness have to be used as coordinates in structure stability diagrams to delineate and predict successfully crystal structure.[45] Chemical hardness (or energy gap) alone is not so successful for this purpose.[46]

The maximum hardness principle as discussed in refs 12 and 13 is for one system only. We are comparing the hardnesses of one system in one state with the same system in another state. A serious question arises in that, when we apply the principle, often we are actually comparing the hardnesses of different systems. The external potential is not the same anymore. Does this nullify our efforts to make the maximum hardness principle useful? Not necessarily. The maximum hardness principle was originally drawn from empirical comparisons between different compounds. We ordinarily apply the principle only to closely related systems through which the external potential change is regular. Change in potential is substantially offset by change in chemical potential. On the basis of the empirical evidence we have surveyed, we believe that a more general maximum hardness principle probably exists, justifying comparison of hardnesses between different external potentials. The close relationship between HOMO–LUMO gap and stability is perhaps the strongest evidence of the existence of such a principle.

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