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A Frontier Orbital Density Functional Approach to Polarizability, Hardness, Electronegativity, and Covalent Radius of Atomic Systems

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The Frontier orbital approach,[1] well-known for providing improved understanding of chemical reactivity, has been rejuvenated[2] through reinterpretation and rationalization within the framework of density functional theory (DFT).[3,4] We here demonstrate that the DFT-based frontier orbitals can play an important role also in the prediction of a number of ground state atomic properties such as polarizability, hardness, electronegativity, and covalent radius, which have attracted considerable attention[5] recently.

The single-particle framework used here for obtaining the highest occupied (HOMO) and lowest unoccupied (LUMO) frontier orbitals is the orbital-based spin-polarized version of DFT, where one solves the single-particle Kohn–Sham[3,4] equation given by (in atomic units)

$$[-(1/2)\nabla^2 + v_{\text{eff}}(\mathbf{r};\{\rho_\sigma\})]\psi_{i\sigma}(\mathbf{r}) = \epsilon_{i\sigma}\psi_{i\sigma}(\mathbf{r}) \qquad (1)$$

to obtain the electron density $\rho(\mathbf{r}) = \sum_{i,\sigma}\rho_{i\sigma}(\mathbf{r}) = \sum_{i,\sigma}|\psi_{i\sigma}(\mathbf{r})|^2$ for an N-electron system. In this self-consistent procedure, the effective potential, $v_{\text{eff}}(\mathbf{r};\{\rho_\sigma\})$, is contributed by the potential due to the nuclei, the electron cloud, and also the exchange-correlation (XC) effects.

Although it is the total density $\rho(\mathbf{r})$ which has been proved[3] to contain all information in DFT, it may be argued that using the spin orbital $\psi_{i\sigma}(\mathbf{r})$, even only for the HOMO, one can fix the effective potential appearing in eq 1, which in turn determines all the orbitals. Hence it might be possible to conjecture that even only the HOMO density (for real orbitals) should be sufficient to determine all the ground state properties. For noninteracting fermions involving simple potentials, it is even possible[6] to express $\rho(\mathbf{r})$ explicitly in terms of the frontier orbital (HOMO and LUMO) densities. This prompts us to attempt to propose suitable schemes to predict various properties using the HOMO/LUMO frontier orbitals corresponding to a single Kohn–Sham calculation for the neutral atom.

For an atom subjected to an oscillatory electric field, the frequency-dependent polarizability $\alpha(\omega)$, corresponding to the induced dipole moment, can be expressed,[7] neglecting inhomogeneity effects, as

$$\alpha(\omega) = -(8/\omega^2)\int_0^\infty \mathrm{d}r\, r \int_0^\infty \mathrm{d}r'\, r' \int_0^\infty \mathrm{d}q\, \rho(r') \times \sin(qr)\sin(qr')\epsilon^{-1}[q,\omega,\rho(r)] \qquad (2)$$

where ϵ is the frequency (ω) and wavenumber (q) dependent local dielectric function, which can be approximated using the local Drude ansatz,[7] as $\epsilon(r) = [1 - \omega_0^2(r)/\omega^2]$, and hence the polarizability given by eq 2 becomes $\alpha(\omega) = \int \mathrm{d}r\, \rho(r)/[\omega_0^2(r) - \omega^2]$. Here $\omega_0(r)$ is a suitable characteristic local frequency, which can be chosen[7] to be the single-particle frequency $\omega_{\text{sp}}(r)$ defined as $\omega_{\text{sp}}^2(r) = (1/r)(\mathrm{d}V/\mathrm{d}r)$ in terms of a local potential $V(r)$. With these approximations and writing $V(r) = (Z/r)\psi(r)$, where Z is the nuclear charge of the atom, the static ($\omega = 0$) polarizability is given by $\alpha = (1/Z)\int \mathrm{d}r\, \rho(r)r^3/[\psi(r) - r\psi'(r)]$. For a neutral atom, $[\rho(r)/Z] = [\rho(r)/N]$ represents the density normalized to unity, and we propose to replace this quantity by $\rho_{\text{HOMO}}(r)$ (an effective HOMO density). The screening function $\psi(r)$ approaches unity as $r \to 0$ and Z^{-1} as $r \to \infty$. For simplicity, we replace $\psi(r)$ by a constant which can be interpreted as the use of mean value theorem to take the function involving $\psi(r)$ outside of the integral and hence obtain the simplified expression for polarizability α given by

$$\alpha = k_\alpha \int \mathrm{d}r\, \rho_{\text{HOMO}}(r)r^3 = k_\alpha \langle r^3\rangle_{\text{HOMO}} \qquad (3)$$

where k_α is an empirical constant.

It is also possible[8] to express the polarizability in terms of the expectation values using the Fukui function[1,4] or the HOMO density as $\alpha = (1/6\eta)\int \mathrm{d}r\, r^2 \rho_{\text{HOMO}}(r)$, where η is the hardness parameter defined[9] as $\eta = (1/2)(\partial^2E/\partial N^2)$. This clearly demonstrates an inverse relation between hardness[9] and the polarizability, and a comparison with eq 3 enables one to express η in terms of the ratio of two expectation values, viz.,

$$\eta = k_\eta \langle r^2\rangle_{\text{HOMO}}/\langle r^3\rangle_{\text{HOMO}} \qquad (4)$$

where k_η is an empirical constant. An inverse relation has also been demonstrated[5d] between the cube root of polarizability and the electronegativity[10] $\chi = -(\partial E/\partial N)$. Thus we propose in view of eq 3 a relation for the calculation of electronegativity given by

$$\chi = k_\chi/[\langle r^3\rangle_{\text{HOMO}}]^{1/3} \qquad (5)$$

We now consider the classical electrostatic potential[11] (ESP) $\phi_-(r) = Z/r - \int \mathrm{d}\mathbf{r}'\, \rho(r')/|\mathbf{r} - \mathbf{r}'|$ of an atomic negative ion, which is positive near the nucleus, but crosses to negative values as r increases, finally passing through a negative minimum. While the position of this minimum has been identified[11] with the ionic radius of the negative ion, we conjecture that the crossing point of the same ESP $\phi_-(r)$ can provide an estimate of the covalent radius (R_0) of the corresponding neutral atom. For simplicity, we propose to mimic the negative ion electron density by adding to the neutral atom electron density an effective LUMO density corresponding to a suitable combination of a few LUMOs of the neutral atom. From $\phi_-(r)$ corresponding to this density, R_0 is determined by the solution of the equation $\phi_-(R_0) = 0$. At $r = R_0$, the ESP of the neutral atom is equal to the Coulomb potential due to the effective LUMO charge density, which is obtained here as the average of the two lowest unoccupied orbital densities (e.g., n $\mathrm{p}_\downarrow$ and $(n + 1)$ $\mathrm{s}_\uparrow$ orbitals when the highest occupied one is n $\mathrm{p}_\uparrow$ or partially filled n $\mathrm{p}_\downarrow$).

We have solved the Kohn–Sham equation (1) with local spin density approximation[12] for the XC potential for a number of atoms (main group elements). The polarizability, hardness, and electronegativity values are then calculated through eqs 3, 4, and 5, respectively, using simple expectation values in terms of the HOMO densities. The empirical constants k_α, k_η, and k_χ are obtained by minimizing the standard deviations between the

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(1) Fukui, K. *Science* **1982,** *218,* 747.

(2) Parr, R. G.; Yang, W. *J. Am. Chem. Soc.* **1984,** *106,* 4049.

(3) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964,** *136,* B864. Kohn, W.; Sham, L. J. *Phys. Rev.* **1965,** *140,* A1133.

(4) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(5) (a) Ghanty, T. K.; Ghosh, S. K. *J. Phys. Chem.* **1993,** *97,* 4951. (b) Rosseinsky, D. R. *J. Am. Chem. Soc.* **1994,** *116,* 1063. (c) Ganguly, P. *J. Am. Chem. Soc.* **1993,** *115,* 9287. (d) Nagle, J. K. *J. Am. Chem. Soc.* **1990,** *112,* 4741.

(6) Dawson, K. A.; March, N. H. *Phys. Lett.* **1983,** *A96,* 460; **1984,** *A106,* 161. Cugnon, J.; Harouna, O. *Europhys. Lett.* **1986,** *1,* 545.

(7) Brandt, W.; Lundqvist, S. *Phys. Rev.* **1965,** *139,* A612. Brandt, W.; Eder, L.; Lundqvist, S. *J. Quant. Spectrosc. Radiat. Transfer* **1967,** *7,* 185. Dimitrieva, I. K.; Plindov, G. I. *Phys. Sci.* **1983,** *27,* 402.

(8) (a) Vela, A.; Gazquez, J. L. *J. Am. Chem. Soc.* **1990,** *112,* 1490. (b) Ghanty, T. K.; Ghosh, S. K. *J. Phys. Chem.*, in press.

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

(10) For recent reviews, see: Sen, K. D., Jorgensen, C. K., Eds.; Electronegativity. *Structure and Bonding*; Springer-Verlag: Berlin, 1987; Vol. 66.

(11) Sen, K. D.; Politzer, P. *J. Chem. Phys.* **1989,** *90,* 4370.

(12) Perdew, J. P.; Zunger, A. *Phys. Rev.* **1981,** *B23,* 5048.

0002-7863/94/1516-8801$04.50/0

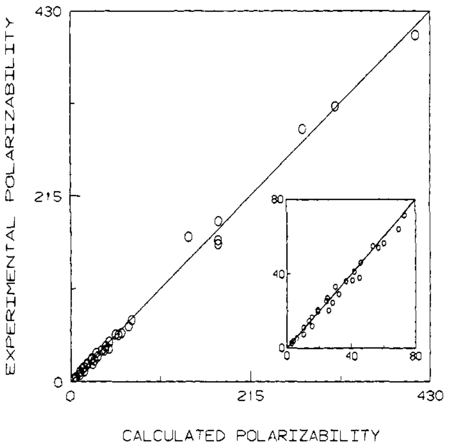

Figure 1. Plot of experimental vs calculated values of atomic polarizability (in atomic units).

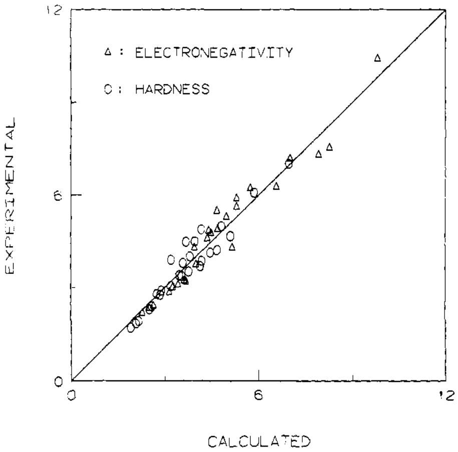

Figure 2. Plot of experimental vs calculated values of atomic hardness and electronegativity (in eV).

experimental and calculated values of the respective quantities for the atoms considered.

For the calculation of polarizability, we obtain $\langle r^3\rangle_{\mathrm{HOMO}}$ using an effective HOMO density, since the contributions from perturbation of all the outermost orbitals are expected to be significant. For this purpose, we first take the average of the up- and down-spin results for each orbital and then use an occupation number weighted average of the outermost s and p orbitals. The plot of the experimental polarizabilities[13] against the calculated ones (with $k_\alpha = 1.48$) in Figure 1 shows excellent agreement. A linear least squares fit of the two results corresponds to a correlation coefficient of 0.997. (It may be noted that lines drawn in the figures here correspond to perfect agreement and not least squares fit.)

For the calculation of hardness and electronegativity, we have used only the outermost HOMO. This is motivated by the fact that the change in occupation number due to change in N involves mainly this HOMO (e.g., in the frozen core approximation). The hardness values calculated using eq 4 with the parameter k_η as 0.50 plotted against the experimental values[4] (obtained from ionization potential and electron affinity data) in Figure 2 show good agreement. The electronegativity values obtained from eq 5 also agree very well with the experimental values[4] plotted in the same figure. The correlation coefficients corresponding to a linear least squares fit for η and χ are 0.959 and 0.974, respectively. It is interesting to note that the optimum value 0.54 of the empirical constant k_χ is very close to that of k_η (=0.50).

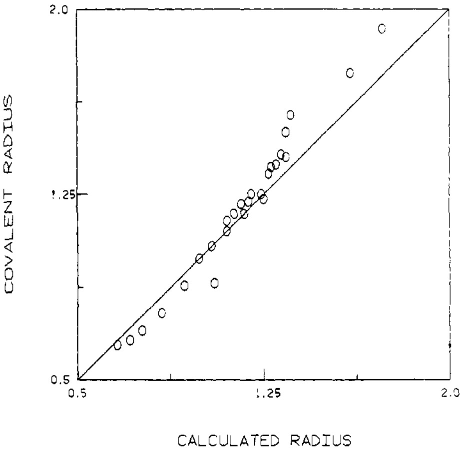

Figure 3. Plot of standard covalent radius vs calculated radius of atoms (in Å).

The values of the radii calculated through the present scheme are plotted in Figure 3 against the standard values of covalent radii from the literature.[14] There is no empirical parameter for the radius, and the correlation coefficient of a linear least squares fit is 0.980. The estimates of the negative ion radii from the positions of the minima of the present $\phi_-(r)$ also agree quite well[8b] with those obtained[11] from the exact ESP of the respective ions. (The inert gas atoms have been excluded for η, χ, and R_0.)

Although the present calculations cover only the main group elements, the formalism is general and is applicable to transition elements as well. The effective HOMO density for polarizability, however, is to be obtained by averaging the highest occupied d orbital (which is close in energy) with the ones already mentioned. It may also be noted that even the SCF orbitals from wave function theory can be employed in the present prescription to obtain qualitatively similar results. Of particular interest is the applicability of the scheme to the case of the hydrogen atom. Using $\langle r^3\rangle = 7.5a_0^3$ and $\langle r^2\rangle = 3a_0^2$ corresponding to the exact 1s orbital density, the predicted values of η and χ agree very well with the actual results. The calculated value of α is, however, somewhat overestimated, which might be attributed to the fact that an effective HOMO density is not employed here.

DFT has been well-known for its success in providing foundation to many widely used chemical concepts including electronegativity[4] and hardness.[15] It has also led to generalized electronegativity equalization procedures[16] for the study of chemical binding in molecular systems. In the present work, through simple expectation values involving the frontier orbitals of DFT, quite good prediction for several global atomic properties has been shown to be possible. Although alternative (DFT-based) prescriptions have been proposed for polarizability,[8] hardness,[17] and the radius,[18] the predictions of the present approach involving the frontier orbitals and requiring only a single calculation for the neutral atom show better correlation with the standard results. Extensions of the present schemes to atomic clusters and molecular systems are straightforward and would be of considerable interest.

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(13) Miller, T. H.; Bederson, B. *Adv. At. Mol. Phys.* **1977**, *13*, 1. Fricke, B. *J. Chem. Phys.* **1986**, *84*, 862.

(14) Dean, J. A., Ed. *Lange's Handbook of Chemistry*, 13th ed., McGraw Hill: New York, 1985.

(15) Berkowitz, M.; Ghosh, S. K.; Parr, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 6811. Chattaraj, P. K.; Parr, R. G. *Struct. Bonding* **1993**, *80*, 11. Nalewajski, R. F. *Struct. Bonding* **1993**, *80*, 115.

(16) Ghanty, T. K.; Ghosh, S. K. *J. Am. Chem. Soc.* **1994**, *116*, 3943. Ghanty, T. K.; Ghosh, S. K. *J. Phys. Chem.* **1994**, *98*, 1840; **1991**, *95*, 6512.

(17) Gazquez, J. L.; Vela, A.; Galvan, M. *Struct. Bonding* **1987**, *66*, 79. Harbola, M. K.; Parr, R. G.; Lee, C. *J. Chem. Phys.* **1991**, *94*, 6055.

(18) Politzer, P.; Parr, R. G.; Murphy, D. R. *J. Chem. Phys.* **1983**, *79*, 3859.