

Relating polarizability to volume, ionization energy, electronegativity, hardness, moments of momentum, and other molecular properties

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Semiquantitative relationships between the mean static dipole polarizability and other molecular properties such as the volume, ionization energy, electronegativity, hardness, and moments of momentum are explored. The relationships are tested using density functional theory computations on the 1641 neutral, ground-state, organic molecules in the TABS database. The best polarizability approximations have median errors under 5%. © 2014 AIP Publishing LLC.
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I. INTRODUCTION

Much effort has been devoted to finding approximations to the mean static dipole polarizability α of a molecule in terms of other, usually more easily accessible, properties of the molecule such as the number of electrons N , number of valence electrons N_v , characteristic length R , size, volume V , ionization energy I , electronegativity χ , and hardness η among others. A terse summary of a representative selection of such work follows.

A very basic observation¹ is that the polarizability generally increases with the number of (valence) electrons. Of course, there will be many exceptions; for example, atomic polarizabilities decrease as one moves from left to right in a fixed row of the Periodic Table.^{2–4}

There have been many attempts to relate the polarizability to hardness and electronegativity.^{5–17} These studies most often use values of hardness and electronegativity as prescribed by qualitative density functional theory (DFT).¹⁸ Some of these studies find a correlation between α and a power of $1/\eta$.

A connection between the ionization energy and the polarizability of an atom has been discussed both numerically^{4,19,20} and formally^{10,21,22} at the level of a Thomas-Fermi-like model. Correlations between α and inverse powers of I have been noted. The second ionization energy I_2 is sometimes involved in the correlations.^{4,10}

Connections between the polarizability and powers of a characteristic length have been sought for more than 90 years;²³ a review of older work is available.²⁴ The mean value $\langle r^2 \rangle$ of the square of the electron distance from an origin, typically the center of mass or electronic charge, is sometimes used as a measure of size.^{25–27} Relationships between the polarizability and molecular size can be based on the Kirkwood approximation^{28,29} which indicates a proportionality between α and $\langle r^2 \rangle^2/N$.

The polarizability of a conducting sphere of radius R is proportional to the volume of the sphere.^{29,30} The same result applies to an atom within an electron gas model.²¹ Correla-

tions between the molecular polarizability and volume have been discussed frequently.^{31–37}

However, much of this prior work has suffered from the use of too crude a model for the computation of the molecular volume and/or hardness, from inaccuracies and inconsistencies in the polarizability data, and from the use of small data sets. Moreover, a significant fraction of past work has focused on atoms. In this work, we perform DFT computations on previously reported structures³⁸ to create a set of consistent data for 1641 neutral molecules in their ground states. This data set is used to investigate relationships between the polarizability and other properties.

A brief summary of computational details in Sec. II is followed by a discussion of relationships between polarizabilities and other molecular properties in Sec. III and some concluding remarks in Sec. IV. Atomic units are used throughout.

II. COMPUTATIONAL DETAILS

Reliable examination of relationships among molecular properties requires a balanced, consistent, moderately large, and reasonably accurate set of data. We started with the TABS database³⁸ of 1641 minimum energy structures all obtained by computations with the B3LYP hybrid density functional^{39–41} and the augmented, correlation consistent, polarized, valence triple-zeta (aug-cc-pVTZ) basis set.^{42,43} The molecules in the TABS database³⁸ contain 17 atoms on average and are all organic. Thus they contain at least one C atom and may have one or more H, N, O, F, S, Cl, and Br atoms. The TABS database contains at least 25 molecules representing each of 24 functional categories. Total and orbital energies for these molecules are already available.³⁸ The molecular volume is not uniquely defined; we follow Bader *et al.*^{44,45} who defined it to be the volume contained by the $0.001 a_0^{-3}$ isodensity surface of the electron density. This molecular volume, the mean value $\langle r^2 \rangle$, and some moments, $\langle p^k \rangle$, of the electron momentum density⁴⁶ were already computed for the TABS database in previous work.⁴⁷

We used Gaussian-03⁴⁸ to calculate the polarizability and vertical ionization potential at the same level for all 1641 structures. Spin-unrestricted calculations were used for the

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open-shell cations. Use of a range-separated functional would probably have lead to more accurate polarizabilities. However, using a model chemistry⁴⁹ (a consistent method and basis set) for all properties is essential because our focus is on establishing relationships among molecular properties.

III. RESULTS AND DISCUSSION

Before turning to polarizabilities, we first examine vertical ionization energies for the molecules in the TABS database. Janak's theorem⁵⁰ in DFT or Koopmans' theorem⁵¹ in Hartree-Fock theory tells us that a useful approximation is given by $I \approx I_0 = -\epsilon_{\text{HOMO}}$ in terms of the energy ϵ_{HOMO} of the highest occupied molecular orbital (HOMO). Several authors^{52–54} have noticed that this approximation can be improved by an empirical fit to the linear equation

$$I \approx aI_0 + b, \quad (1)$$

in which a and b are parameters. The effectiveness of this fit for the TABS database can be seen in Fig. 1. A linear least-squares fit of our computed vertical ionization energies gives

$$I \approx 1.1312I_0 + 0.0481. \quad (2)$$

This fit leads to a root-mean-square percentage error (RM-SPE) of only 2.8%.

Consider correlations involving the electronegativity and hardness. Parr *et al.*⁵⁵ defined the electronegativity as the partial derivative of the energy with respect to the number of electrons at constant external potential v ; thus, they wrote

$$\chi = -(\partial E / \partial N)_v. \quad (3)$$

A three-point finite-difference approximation to the above derivative leads to the Mulliken electronegativity:

$$\chi = (I + A)/2, \quad (4)$$

in which I is the vertical ionization energy and A is the vertical electron affinity. A further simplification is to approximate I and A in terms of the frontier orbital energies. Thus,

$$\chi \approx \chi_0 = -(\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}})/2, \quad (5)$$

in which ϵ_{LUMO} is the energy of the lowest unoccupied molecular orbital (LUMO). Correlations between α and an inverse power of χ_0 are very weak; the best one, $\alpha \approx a/\chi_0^2$, leads to a RM-SPE of 48%.

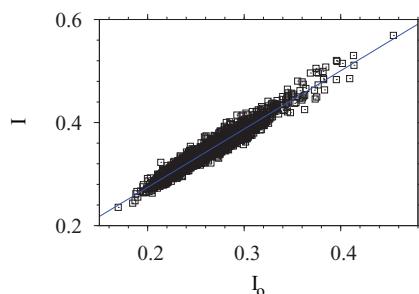


FIG. 1. Vertical ionization energy I as a function of the orbital approximation I_0 . All quantities are in atomic units. The solid line is Eq. (2).

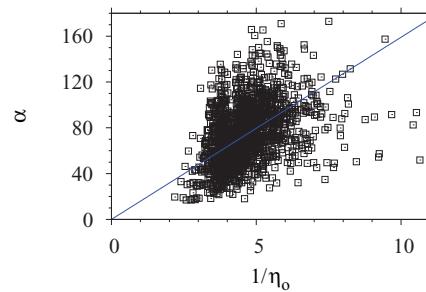


FIG. 2. Polarizability α as a function of the reciprocal hardness, $1/\eta_0$. All quantities are in atomic units. The solid line is Eq. (10).

Parr and Pearson⁵⁶ defined the hardness as the second partial derivative of the energy with respect to the number of electrons at constant external potential v ; thus, they advocate

$$\eta = (\partial^2 E / \partial N^2)_v. \quad (6)$$

A factor of 1/2 was present on the right-hand-side of Eq. (6) in their original paper⁵⁶ but it has since been dropped.¹⁶ A three-point finite-difference approximation to the second derivative leads to

$$\eta = I - A. \quad (7)$$

Cárdenas *et al.*¹⁷ questioned whether a negative electron affinity should be used in Eq. (7) and examined whether it was preferable to use

$$\eta = I - \max[A, 0] \quad (8)$$

instead. However, they did not find enough evidence in unequivocal favor of Eq. (8) and continue to use the usual Eq. (7) arguing that there is no harm in using negative values of A to compute the hardness. Using orbital energies leads to the hardness being approximated by the gap between the unoccupied and occupied orbitals; thus,

$$\eta \approx \eta_0 = \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}. \quad (9)$$

As in earlier work,⁵⁷ we could not find a good correlation between α and a power of η_0 . The least bad one was an inverse proportionality of the form

$$\alpha \approx 15.908/\eta_0. \quad (10)$$

This correlation, shown in Fig. 2, leads to a RM-SPE of 43%.

Using Eq. (7) is not always straightforward because both the calculation and measurement of accurate electron affinities can be difficult. Tozer and De Proft⁵⁸ proposed that negative electron affinities of neutral systems be obtained from

$$A \approx -(\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}}) - I \quad (11)$$

which can be rewritten as

$$A \approx 2\chi_0 - I. \quad (12)$$

They justify Eq. (11) in terms of integer discontinuities in the exact exchange-correlation potential. Even though their arguments are not appropriate for hybrid functionals, Eq. (11) works moderately well even in such cases. It is not unreasonable to estimate the hardness of any neutral closed-shell

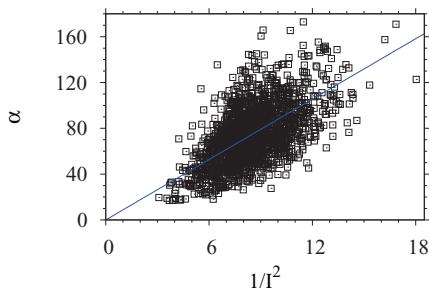


FIG. 3. Polarizability α as a function of $1/I^2$. All quantities are in atomic units. The solid line is Eq. (15).

system by combining Eq. (12) with Eq. (7) to write

$$\eta \approx \eta_1 = 2(I - \chi_0). \quad (13)$$

Unfortunately, using η_1 instead of η_0 does not yield any meaningful improvement to the correlation of Eq. (10). Thus, the best fit that we could find was

$$\alpha \approx 29.068/\eta_1. \quad (14)$$

It has a RMSPE of 39%. Other inverse powers of η_1 lead to even worse correlations.

Next, consider correlations with vertical ionization energies. Previous work on atoms^{19,20} suggests that the polarizability varies roughly as $1/I^3$. However, the best linear fit of α to a power of I for the TABS database is obtained with

$$\alpha \approx 8.7905/I^2. \quad (15)$$

This correlation, shown in Fig. 3, leads to a RMSPE of 36% and is not a significant improvement over the correlations between polarizability and hardness considered above.

Next, consider correlations between the polarizability and the molecular size. The mean value of the square of the distance between an electron and the origin of the molecular coordinate system is given by

$$\langle r^2 \rangle = \sum_{i=1}^N \langle r_i^2 \rangle, \quad (16)$$

in which the sum is over the N electrons. The diamagnetic susceptibility⁵⁹ is proportional to $\langle r^2 \rangle$. Clearly, the value depends upon the choice of coordinate origin. In a molecule, two reasonable choices of origin are the center of mass and the center of nuclear charge. We chose the latter. Then $\mathcal{R} = \langle r^2 \rangle^{1/2}$ serves as a characteristic length. Dimensional considerations suggest a correlation between α and \mathcal{R}^3 although early work²⁴ invariably found a correlation with a higher power, typically four, of a characteristic length. To our surprise, we found that the most accurate least-squares fit of α to a multiple of a power of \mathcal{R} involves just the first power of \mathcal{R} as follows:

$$\alpha \approx 2.4741 \langle r^2 \rangle^{1/2}. \quad (17)$$

This correlation, shown in Fig. 4, leads to a RMSPE of 18%. The egregious outliers in Fig. 4 are molecules, like substituted non-branched alkanes, in which the electron density has a noticeably different spatial extent in one direction. Clearly, \mathcal{R} is

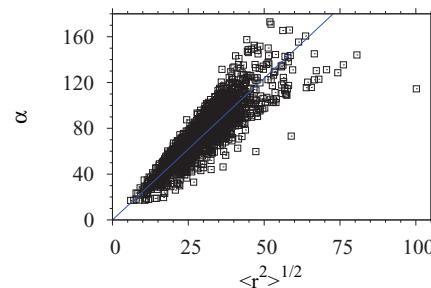


FIG. 4. Polarizability α as a function of the characteristic length, $\mathcal{R} = \langle r^2 \rangle^{1/2}$. All quantities are in atomic units. The solid line is Eq. (17).

not a good measure of molecular size in molecules with an electron density that is elongated in one direction.

Very recently,⁴⁷ we found that molecular size correlates well with the $\langle 1/p \rangle$ moment of the electron momentum density.⁴⁶ Within the impulse approximation,^{46,60} the moment $\langle 1/p \rangle$ is twice the peak height of the isotropic Compton profile $J(q)$. The latter is the intensity of Compton scattering at wavelengths shifted, by a Doppler broadening-like mechanism, from the wavelength at which Compton scattering by a motionless electron would be predicted.⁴⁶ In particular, we found that \mathcal{R} is approximately proportional to the momentum moment $\langle 1/p \rangle = 2J(0)$. In view of Eq. (17), these properties also correlate with α as follows:

$$\alpha \approx 1.7330 \langle 1/p \rangle = 3.4660 J(0). \quad (18)$$

The correlation of Eq. (18) leads to a RMSPE of 17%.

Next, we turn to correlations between polarizability and volume. A fit to the TABS database yields

$$\alpha \approx 0.084852 V. \quad (19)$$

The correlation of Eq. (19), shown in Fig. 5, has a RMSPE of 14.8%. It appears that the polarizability grows a bit faster than the volume and the best fit to $V^{4/3}$ is given by

$$\alpha \approx 0.0084161 V^{4/3}. \quad (20)$$

Eq. (20) has a smaller RMSPE of 12% but almost the same absolute RMS error as Eq. (19). Figure 5 shows quite clearly that α is not a smooth function of V . Hence, it is not likely that significant improvements can be obtained by using an even more complicated function of V on the right hand side of Eq. (20).

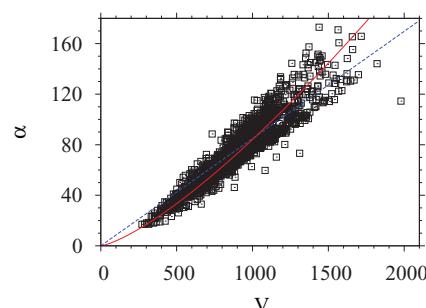


FIG. 5. Polarizability α as a function of the volume V . All quantities are in atomic units. The dashed (blue) line is Eq. (19) and the solid (red) line is Eq. (20).

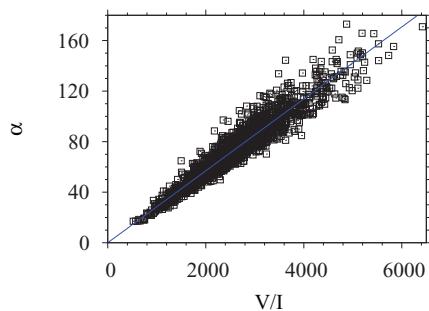


FIG. 6. Polarizability α as a function of V/I . All quantities are in atomic units. The solid line is Eq. (22).

Recently, we found that the correlation between V and the momentum moment $\langle 1/p^2 \rangle$ was unexpectedly strong.⁴⁷ Thus, it is not surprising to find that the approximation

$$\alpha \approx 1.1646 \langle 1/p^2 \rangle \quad (21)$$

has a RMSPE of 13.2%, comparable to but a bit better than that of Eq. (19). The moment $\langle 1/p^2 \rangle$ can be obtained from an experimentally measured Compton profile $J(q)$ via a sum rule.⁶¹

Finally, we examined correlations of α with variables composed from two or more properties. Such variables can be very helpful even if they usually do not have an independent physical interpretation. A small selected subset of the best of these correlations is summarized next. A correlation better than any of those considered above is obtained with respect to V/I ; thus the fit given by

$$\alpha \approx 0.028463V/I \quad (22)$$

has a RMSPE of 9.7%. It is illustrated in Fig. 6.

Even better results are obtained by using the novel relationship given by

$$\alpha \approx 0.031201V/\eta_1. \quad (23)$$

It has a RMSPE of 8.0%. Our very best results are obtained from the new approximation given by

$$\alpha \approx 0.040288V/\eta_1^{3/4}. \quad (24)$$

This correlation, illustrated in Fig. 7, has a RMSPE of 7.3% and a median absolute percent error of only 4.5%. An approximation of very similar quality can be obtained by changing the power of η on the right hand side of Eq. (24) from 3/4 to 2/3 with a corresponding change to the proportionality con-

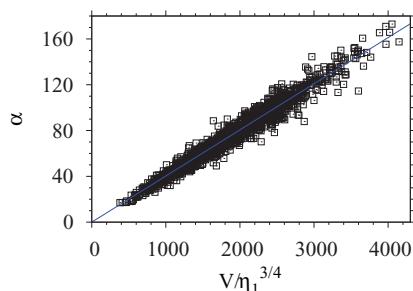


FIG. 7. Polarizability α as a function of $V/\eta_1^{3/4}$. All quantities are in atomic units. The solid line is Eq. (24).

stant. Perhaps a qualitative DFT argument can be concocted to justify Eq. (24). Inserting Eq. (13) into Eq. (24) leads to an equivalent form of our best correlation given by

$$\alpha \approx 0.023955V/(I - \chi_0)^{3/4}. \quad (25)$$

The reoptimized analogs of Eqs. (22)–(24) with V replaced by $\langle 1/p^2 \rangle$ are of similar but slightly worse quality. For example, the correlation given by

$$\alpha \approx 0.55175\langle 1/p^2 \rangle/\eta_1^{3/4} \quad (26)$$

or, equivalently, by

$$\alpha \approx 0.32807\langle 1/p^2 \rangle/(I - \chi_0)^{3/4} \quad (27)$$

has a RMSPE of 7.7% and a median absolute percent error of 4.8%.

IV. CONCLUDING REMARKS

The use of a large and consistent set of data enabled us to evaluate with confidence the quality of many old and some new relationships between polarizabilities and other molecular properties. Direct correlations between polarizability and electronegativity, hardness, or ionization energy are not particularly good. The polarizability correlates better with size as measured by $\langle r^2 \rangle^{1/2}$ or by the peak height of the Compton profile. The polarizability correlates better still with volume and with the momentum moment $\langle 1/p^2 \rangle$. Semiquantitative correlations are found only when composite variables are used. The two best correlations that we found, Eqs. (24)–(27), lead to median absolute errors under 5%.

If a quick estimate of a polarizability is needed for a molecule, then one should use the best relationship in this work for which one has the requisite data. All the relationships discussed in this paper are more closely satisfied if attention is restricted to chemically similar molecules. Hence, to obtain better accuracy, one should recalibrate the chosen relationship for a small set of molecules closely related to the molecule of interest before applying the approximation. For a bit more accuracy, one can use additive models^{62,63} based on atom types⁶⁴ or on molecular fragments.⁶⁵

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