Comparative study of unscreened and screened molecular static linear polarizability in the Hartree-Fock, hybrid-density functional, and density functional models

Rajendra R. Zope\textsuperscript{1,2}, Tunna Baruah\textsuperscript{1}, Mark R. Pederson\textsuperscript{3}, and B. I. Dunlap\textsuperscript{4}

\textsuperscript{1}Department of Physics, University of Texas at El Paso, El Paso, Texas 79959
\textsuperscript{2}Department of Electrical and Computer Engineering, Howard university, Washington, DC 20059
\textsuperscript{3}Center for Computational Materials Science, Code 6392, Naval Research Laboratory, Washington DC 20375-5345 and
\textsuperscript{4}Theoretical Chemistry Section, Naval Research Laboratory, Washington DC 20375-5345

(Dated: September 6, 2018)

Abstract

The sum-over-states (SOS) polarizabilities are calculated within approximate mean-field electron theories such as the Hartree-Fock approximation and density functional models using the eigenvalues and orbitals obtained from the self-consistent solution of the single-particle equations. The SOS polarizabilities are then compared with those calculated using the finite-field (FF) method. Three widely used mean-field models are used: (1) the Hartree-Fock (HF) method, (2) the three parameter hybrid generalized gradient approximation (GGA) (B3LYP), and (3) the parameter-free generalized gradient approximation due to Perdew-Burke-Ernzerhof (PBE). The comparison is carried out for polarizabilities of 142 molecules calculated using the 6-311++G(d,p) basis set at the geometries optimized at the B3LYP/6-311G** level. The results show that the SOS method almost always overestimates the FF polarizabilities in the PBE and B3LYP models. This trend is reversed in the HF method. A few exceptions to these trends are found. The mean absolute errors (MAE) in the screened (FF) and unscreened (SOS) polarizability are 0.78 \, \text{Å}^3, 1.87 \, \text{Å}^3, and 3.44 \, \text{Å}^3 for the HF, B3LYP and PBE-GGA methods, respectively. Finally, a simple scheme is devised to obtain FF quality polarizability from the SOS polarizability.

PACS numbers: 31.15.Ar, 31.70.Hq, 34.70.+e, 84.60.Jt, 87.15.Mi

Keywords: polarizability, sum over states, finite field
In this paper, we examine sum-over-states (SOS) and finite-field (FF) polarizabilities for Hartree-Fock (HF), a hybrid density-functional B3LYP [1, 2], and a generalized gradient approximation (GGA) pure density-functional, Perdew-Burke-Ernzerhof (PBE) [3], for a large set of molecules. These three are popular independent-particle models that are routinely used to study the electronic structure of molecules. We discuss the relationship between the SOS polarizabilities and the one-electron eigenvalues of these mean-field methods. We then devise a simple empirical scheme to obtain finite-field quality estimate of the polarizability from the HF and PBE models. We also investigate the differences in the predictions of polarizabilities from SOS and FF methods in the above popular single-particle methods.

When a molecule is placed in a static electric field $\vec{F}$, the electronic charge of the molecule redistributes. This response is characterized by the polarizability of the molecule. The molecular energy $E$ in the presence of a small external field can be expressed as a perturbative series in power of $\vec{F}$ as

$$E = E_0 + \sum_i \frac{\partial E}{\partial F_i} \bigg|_{\vec{F} = 0} F_i + \frac{1}{2!} \sum_{ij} \frac{\partial^2 E}{\partial F_i \partial F_j} \bigg|_{\vec{F} = 0} F_i F_j + \frac{1}{3!} \sum_{ijk} \frac{\partial^3 E}{\partial F_i \partial F_j \partial F_k} \bigg|_{\vec{F} = 0} F_i F_j F_k + \ldots$$

where, $E_0$ is the total energy of the molecule in the absence of the external electric field, $\mu$ is the induced dipole moment, $\alpha$ is the linear polarizability, and $\beta$ is the first hyperpolarizability; the indices i,j,k denote the Cartesian components. The calculation of the linear polarizability $\alpha_{ij}$, which is the topic of the present manuscript, requires calculation of the second derivative of the total molecular energy with respect to applied field. The $\alpha_{ij}$ terms can be calculated using perturbation theory or by finite difference technique by using the total energies calculated at various field strengths. A summary of various methods for practical calculations of polarizabilities can be found in several review articles [4, 5].

Using standard time-independent perturbation theory, one can obtain the well-known SOS expression (see, for example Bartlett and Sekino in Ref.5). The SOS expression for a diagonal element of the polarizability tensor is given by

$$\alpha_{zz} = \sum_{k \neq 0}^{\infty} \frac{\langle \Psi_0 | \hat{z} | \Psi_k \rangle \langle \Psi_k | \hat{z} | \Psi_0 \rangle}{E_k - E_0}$$

where, $\hat{z}$ is the electric field operator, $\Psi_0$ is the ground state wavefunction, and $E_k$ is the $k$th excited state energy.
Here, $E_0$ is the ground-state electronic energy and $E_k$ is the energy of the k-th excited state and and $\Psi_0$ is the ground-state wavefunction and $\Psi_k$ is the wavefunction of the k-th excited state. The matrix element $\langle \Psi_0 | \hat{z} | \Psi_k \rangle$ is the $z^{th}$ component of the transition dipole moment. Thus, knowledge of the excitation energies and the transition dipole moments can be used to compute the polarizability using the SOS method. The summation in the SOS expression (Eq. (3)) is over all excited states. One major advantage of the SOS method is that the transitions that make significant contributions to the polarizability can be identified. If the perturbation is small then one expects the largest term in this expression to be the first because it has the smallest energy denominator. In mean-field theories this energy difference is often approximated by the difference between the energy of highest-occupied molecular orbital (HOMO) and the energy of the lowest unoccupied molecular orbital (LUMO). In the following we call the exact first energy difference, $E_1 - E_0$, and approximations to it the HOMO-LUMO gap.

Exact polarizibilities can also be obtained using small finite fields. In the finite field (FF) method the molecular Schrödinger equation is solved for different directions and magnitudes of the applied electric field and finite differences are used to calculate the components, $\alpha_{ij}$, of the polarizability tensor. The polarizability matrix elements can be obtained using a least square fit to the total molecular energies or by using a suitable numerical approximation to obtain the second derivative.

The methods for the calculation of the molecular energy by solving Schrödinger equation can be broadly sorted in two classes: the traditional quantum mechanical methods such as the HF method and beyond, and and models based on density functional theory (DFT). In this article, we perform a comparative study of polarizabilities computed using the SOS and finite-field methods. The comparison is carried out for polarizabilities calculated within the HF approximation and two DFT models.

Within mean-field theories such as the HF or DFT, the SOS equation (3) can be written as

$$\alpha_{ij} = 2 \sum_{m}^{\text{unocc.}} \sum_{n}^{\text{occ.}} \frac{\langle \psi_m | p_i | \psi_n \rangle \langle \psi_n | p_j | \psi_m \rangle}{\epsilon_m - \epsilon_n}.$$  

(4)

Here, the $\{\psi\}$ and $\{\epsilon\}$ are the self-consistent molecular orbitals and eigenvalues, respectively. The summation in this expression runs over all occupied and virtual states. In practice, however, only a finite number of virtual states are included since the contributions from
very high energy states are negligible. Hereafter, we shall refer to the Eq. (4) as the sum-over-states SOS expression (and not Eq. (3), which is over fully correlated electronic states) and the polarizability calculated using this equation as the $\alpha_{SOS}$.

The single-particle eigenvalues in Eq. (4) can be viewed as approximations to the excitation energies of the computational model. This expression treats each orbital as responding independently to the applied electric field, but as the orbitals respond to the applied field the self-consistent or mean-field component of the Fock and KS potentials also changes. Eq. (4) uses only the unperturbed eigenfunctions $\psi_m$ and eigenvalues. The additional field-induced electron redistribution, or screening, is missing in the computation of polarizabilities by the SOS method. The $\alpha_{SOS}$ are called the unscreened polarizability.

The self-consistent treatment of field-induced polarization that includes the screening effects can be computed by the FF method. In this method a term ($-\vec{F} \cdot \vec{r}$) that represents interaction between the electrons and the applied field is added to the zero-field, one-body Hamiltonian, and the single-particle equations (Hartree-Fock or Kohn-Sham) are solved self-consistently. The self-consistent procedure takes into account the screening effects or field-induced polarizations. The polarizability is then calculated by numerical differentiation of the energy or dipole moment obtained at various field strengths in limit of vanishing field. As a result of the complete description of the first-order screening effects, the $\alpha_{FF}$ polarizabilities generally are found to be in good agreement with experimental values. Equivalently, the energy derivative required for the polarizability can be computed analytically by differentiation of the field-dependent Hamiltonian. The latter approach is called coupled HF method.

The lack of an appropriate description of the screening effects in the $\alpha_{SOS}$ calculations generally results in $\alpha_{SOS}$ overestimating the experimental polarizabilities and $\alpha_{FF}$ in density-functional methods. Early calculations of Stott and Zaremba showed that the inclusion of screening by self-consistent calculation of polarizabilities of atoms reduces its value by roughly 40%. Later, Mahan also noted that a self-consistent treatment reduced the linear polarizability by about 40% but the next two higher (hyper) polarizabilities are reduced by 2% only. Similar conclusions were drawn by Pederson and Quong, who in their calculation on the $C_{60}$ fullerene found $\alpha_{SOS}$ to be roughly three times larger than the screened $\alpha_{FF}$, with the latter value being in good agreement with experimental measurements. These works show that the inclusion of screening effects is necessary for a satisfactory estimation of
polarizability. The appropriate treatment of screening effects using finite-field or equivalent methods requires full self-consistent solution cannot take advantage of the full unperturbed point-group symmetry. This lack of symmetry can make polarizability calculations computationally intensive for large systems such as carbon fullerenes, quantum dots, finite nanotubes etc. For this reason, simple schemes to correct $\alpha_{\text{SOS}}$ for the screening effects have been devised and applied\[13, 14, 15\]. Recently, Gueorguiev, Pacheco and Tománek have used a similar scheme to calculate polarizabilities of large carbon fullerenes within the tight-binding method.\[15\].

The orbital eigenvalues that are required in the SOS method (Eq. 4) have different interpretations in HF theory and DFT [17]. In HF theory, Koopmans theorem states that the occupied orbital eigenvalues are the negative of unrelaxed ionization energies.\[18\]. On the other hand, in DFT only the highest occupied eigenvalue has a physical interpretation as the negative of the first ionization potential\[19\]. The DFT eigenvalues are the derivatives of the total energy with respect to orbital occupancies\[20\]. The practical DFT applications require approximations to the exchange-correlation functionals that model the exchange-correlations effects that are quantal in origin. Due to the nature of most of these approximate functional forms, the effective potential that an electron experiences is contaminated with self-interaction. Consequently, the negative of the energy eigenvalue of the highest occupied orbital in these approximate schemes often underestimates the first ionization potential. The HOMO-LUMO gap is also underestimated typically by about 30-40\%\[21, 22\] due to the so-called band gap problem\[23, 24\]. In the HF theory, self-Coulomb potential exactly cancels the self-exchange potential for the occupied electrons and hence in the HF model the occupied electrons experience only electronic interactions with the other occupied electrons. Thus HF is self-interaction free for occupied orbitals. The virtual orbitals, however, experience the full electronic interaction with all the occupied electrons. Therefore, the HOMO-LUMO gap in HF theory is usually overestimated.

The unscreened SOS method (Eq. 4) is often used within the HF for qualitative purposes. A better and more appropriate expression in place of the HF eigenvalue differences in the denominator can be obtained based on the following argument. Once the zero-field ground-state HF determinant is found, it is possible to develop a multiconfigurational treatment which is successively more accurate by first constructing one-electron excitations, then two-electron excitations etc. Brillouin’s theorem tells us that there is no coupling between
one-electron excitations and the occupied, zero-field molecular orbitals. When the many-electron field-induced perturbation ($\sum_i \vec{F} \cdot \vec{r}_i$) is added to this Hamiltonian, the only coupling between different zero-field single-electron excitations is due to this term and it is of the form $(\psi_m | \vec{F} \cdot \vec{r} | \psi_n)$ for the excitation which replaces the formerly occupied state $\psi_m$ by $\psi_n$. The energy of this state relative to the ground state is $\epsilon_m - \epsilon_n - \Delta_{mn}$ with $\Delta_{mn}$ a gap reducing correction given by:

$$\Delta_{mn} = (\psi_m^\dagger \psi_m | 1/r_{12} | \psi_n^\dagger \psi_n) - (\psi_m^\dagger \psi_n | 1/r_{12} | \psi_m^\dagger \psi_n)$$

(5)

In the above expression the $\psi_m$ are to be viewed as a product state of the spatial wavefunction and spinor. The second term is zero for spin-flip excitations. So, if a CI approach, with only single excitations, is employed, it is easy to show from perturbation theory that the correct expression for the polarizability within this approximation is not identical to the normal sum of states method because there is a pair-dependent correction to the energy denominators. In other words, rather than Eq. (4), the $\alpha_{SOS}$ should be

$$\alpha_{ij} = 2 \sum_{m}^{\text{unocc.}} \sum_{n}^{\text{occ.}} \frac{\langle \psi_m^\dagger | p_i | \psi_n \rangle < \psi_n^\dagger | p_j | \psi_m \rangle}{\epsilon_m - \epsilon_n - \Delta_{mn}}.$$  

(6)

While the single-electron CI approach is itself an approximation, it is a more proper definition for the unscreened approximation and differs from the standard SOS method used in HF.

As the HOMO-LUMO gap is the lowest of many excitation energies that contribute to $\alpha_{SOS}$, the trend in $\alpha_{SOS}$ in two types of models (HF and DFT) should be, in general, opposite to that observed for the HOMO-LUMO gaps. While the general trends of overestimation and underestimation of $\alpha_{SOS}$ in the HF method and DF based models are to be expected, a detailed comparison on a large set of molecules is necessary to determine if this trend in the two types of models always holds, which partially motivates the present work.

Our interest in the SOS method (Eq. 4) is primarily due to the fact that it is computationally inexpensive to apply, particularly for large, symmetric molecules for which the application of the finite-field method becomes very expensive. The SOS (using Eq. (4)) indeed has been employed in the past to compute the polarizability of carbon fullerenes $^{[13, 14, 15, 16]}$. In these works, the calculated $\alpha_{SOS}$ were scaled using a scaling factor to account for the screening effects. As the point group symmetry of molecules can be efficiently employed in $\alpha_{SOS}$ calculations, Eq. (4) offers a possibility of obtaining estimates of polarizability of
large symmetric molecules that are beyond the reach of the more accurate, but symmetrybreaking, FF method. Our goal is to estimate the polarizabilities of carbon fullerenes, quantum dots, and nanocrystalline materials containing about 1000-2000 atoms by the SOS method. The present work is a detailed investigation to understand the behavior of \( \alpha_{SOS} \) within different computational schemes.

We have chosen a large set of 142 molecules belonging to the extended G2 set of molecules whose geometries are well known. To facilitate the comparison between different single-particle methods, we choose the same set of geometries and basis sets in our polarizability calculations in all models. This eliminates some sources of discrepancy in the comparison of polarizabilities. The geometries of 142 molecules were first optimized using the B3LYP hybrid DFT model using the 6-311G** orbital basis set. B3LYP is one of the most popular hybrid functionals. It contains a weighted mixture of the Becke88 exchange functional, the Lee-Yang-Parr gradient corrected correlation, Vosko-Wilk-Nusair correlation functional, the local-density exchange functional, and HF exchange. The mixing coefficients are determined empirically by fitting to atomization energies. The HF and B3LYP calculations were performed using the Gaussian03 at the Army Research Laboratory while the PBE calculations were performed using the NRLMOL suites of code. The NRLMOL is a massively parallelized suite of codes developed at the Naval Research Laboratory for DFT calculations for molecules. The molecular orbitals in the NRLMOL are expressed as a sum of linear combinations of Gaussian orbitals and the polarizability is computed using the FF method by numerically differentiating the calculated dipole moment at different field strengths/directions. The electric field values are chosen in the step of 0.005 a.u. These values provide reliable estimate of the polarizability. For a recent review on the details of polarizability calculations using the NRLMOL code, we refer the interested reader to Ref. 29. It is well known that for accurate computation of polarizability, well chosen Gaussian basis set augmented with diffused functions is often necessary. In this work, we have used the 6-311++G(d,p) type of basis for all polarizability calculations. This basis was selected on two criteria: (i) it is large enough to provide good accuracy for the polarizability (ii) its availability for all elements that belong to the chosen set of molecules.

The \( \alpha_{SOS} \) and \( \alpha_{FF} \) of 142 molecules calculated within HF, B3LYP, and PBE models are compared in Table I. These are the mean polarizabilities obtained from the trace of the polarizability tensor as \( \alpha = \frac{1}{3} \sum_{i=1}^{3} \alpha_{ii} \). Although the main goal of this work is to compare
screened and unscreened polarizabilities, for completeness we also included in the table the experimental values of polarizabilities for selected molecules. All experimental values are from the CRC Handbook[30]. The overall agreement between theory and experiment is good. There are large differences for some molecules (e.g. ClF\textsubscript{3} which has a large vibrational contribution to polarizability). There are many possible causes for these differences such as temperature effects, basis sets effects and vibrational contributions. Proper treatment of these effects will give better agreement but is outside the scope and purpose of the present paper. Hence we shall not elaborate on the comparison of theoretical and experimental values of polarizability. The comparison of the (unscreened) \( \alpha_{SOS} \) with screened \( \alpha_{FF} \), within the three models show different trends. In the HF method the \( \alpha_{SOS} \) are smaller than the \( \alpha_{FF} \) with the exceptions of the P\textsubscript{2}, CS, COS, and N\textsubscript{2}O molecules. The two values of polarizability for these exceptions are quite close, with the difference for P\textsubscript{2} being the largest. This almost always correct trend of HF polarizabilities is reversed in the parameter-free PBE DFT model. We find no exceptions. In PBE, SOS polarizabilities are always less than FF polarizabilities. The \( \alpha_{SOS} \) in PBE are consistently higher than the \( \alpha_{FF} \) polarizabilities. These trends, as noted earlier, are consistent with the general trend of the HF and PBE models to underestimate and overestimate the HOMO-LUMO energy gap. The \( \alpha_{SOS} \) are also predicted to be larger than \( \alpha_{FF} \) in the B3LYP method. However, the overestimation in the B3LYP model is less than that in the PBE model. The mean absolute error (MAE) calculated as \( MAE = \frac{1}{142} \sum_{i=1}^{142} |\alpha_{SOS} - \alpha_{FF}| \) is reduced from 3.55 Å\textsuperscript{3} for the PBE to 1.95 Å\textsuperscript{3} for the B3LYP functional. The MAE is least in the HF theory, for which the mean error is negative. The hybrid B3LYP functional benefits from the opposite effects of overestimation in pure DF models and underestimation in the HF theory.

TABLE I: The polarizabilities for the set of 142 (extended G2 set) of molecules computed by sum over states and coupled HF methods or finite field within the Hartree-Fock approximation, hybrid B3LYP model and the PBE generalized gradient approximation. The polarizabilities are calculated using the 6-311++G(d,p) at the geometries optimized at B3LYP/6-311G** level. All values are in Å\textsuperscript{3}. I: SOS , II: Coupled HF or finite-field

| Molecule | HF(I) | HF(II) | B3LYP(I) | B3LYP (II) | PBE (I) | PBE (II) | Expt.[30] |
|----------|------|--------|----------|-----------|---------|---------|-----------|
| H\textsubscript{2}    | 0.3  | 0.4    | 0.5      | 0.4       | 0.6     | 0.5     | 0.8       |
| LiH       | 1.9  | 3.2    | 4.0      | 4.2       | 5.5     | 4.7     |           |
| BeH       | 2.2  | 4.2    | 4.4      | 4.5       | 3.2     | 4.7     |           |
| CH        | 1.1  | 1.7    | 2.0      | 1.8       | 2.6     | 1.8     |           |
| Compound                  | 1.1 | 1.5 | 1.8 | 1.6 | 1.6 | 1.7 |
|---------------------------|-----|-----|-----|-----|-----|-----|
| CH$_2(^3B_1)$             | 1.4 | 1.9 | 2.5 | 2.1 | 3.7 | 2.1 |
| CH$_2(^1A_1)$             | 1.4 | 1.8 | 2.2 | 2.0 | 2.2 | 2.0 |
| CH$_3$                    | 1.8 | 2.1 | 2.6 | 2.2 | 3.0 | 2.6 |
| CH$_4$                    | 1.0 | 1.3 | 1.6 | 1.4 | 2.0 | 1.5 |
| NH$_2$                    | 1.3 | 1.6 | 2.1 | 1.8 | 2.4 | 1.8 |
| OH                        | 0.5 | 0.7 | 0.8 | 0.8 | 1.0 | 0.8 |
| H$_2$O                    | 0.8 | 1.0 | 1.2 | 1.1 | 1.5 | 1.1 |
| HF                        | 0.4 | 0.5 | 0.6 | 0.5 | 0.7 | 0.6 |
| Li$_2$                    | 17.7| 30.3| 37.9| 29.3| 57.0| 30.2|
| LiF                       | 0.6 | 0.8 | 1.3 | 1.2 | 1.7 | 1.4 |
| C$_2$H$_2$                | 2.6 | 2.8 | 4.3 | 2.9 | 5.1 | 2.9 |
| C$_2$H$_4$                | 3.1 | 3.8 | 5.1 | 3.8 | 6.1 | 3.8 |
| C$_2$H$_6$                | 3.1 | 3.8 | 5.0 | 4.0 | 5.9 | 4.1 |
| CN                        | 1.6 | 1.9 | 4.3 | 2.9 | 5.9 | 2.7 |
| HCN                       | 2.0 | 2.1 | 3.3 | 2.1 | 3.9 | 2.2 |
| CO                        | 1.4 | 1.6 | 2.5 | 1.7 | 3.0 | 1.8 |
| HCO                       | 1.7 | 2.1 | 3.0 | 2.2 | 3.7 | 2.3 |
| H$_2$CO (formaldehyde)    | 1.8 | 2.2 | 3.1 | 2.3 | 3.8 | 2.4 |
| H$_3$COH                  | 2.1 | 2.6 | 3.4 | 2.8 | 4.1 | 2.9 |
| N$_2$                     | 1.4 | 1.5 | 2.4 | 1.5 | 2.8 | 1.6 |
| N$_2$H$_4$                | 2.3 | 2.8 | 3.8 | 3.1 | 4.5 | 3.2 |
| O$_2$                     | 1.1 | 1.4 | 1.8 | 1.2 | 3.2 | 1.2 |
| H$_2$O$_2$                | 1.4 | 1.8 | 2.4 | 1.9 | 2.9 | 1.9 |
| F$_2$                     | 0.7 | 1.0 | 1.3 | 0.9 | 1.6 | 0.9 |
| CO$_2$                    | 1.9 | 2.0 | 3.4 | 2.2 | 4.2 | 2.2 |
| SiH$_2(^1A_1)$            | 3.2 | 4.4 | 6.0 | 4.5 | 7.9 | 4.6 |
| SiH$_2(^3B_1)$            | 2.6 | 3.7 | 4.7 | 4.0 | 4.3 | 4.1 |
| SiH$_3$                   | 2.9 | 3.9 | 5.1 | 4.2 | 5.0 | 4.3 |
| SiH$_4$                   | 2.9 | 3.7 | 5.0 | 4.0 | 6.2 | 4.2 |
| PH$_2$                    | 2.5 | 3.3 | 4.4 | 3.4 | 5.3 | 3.5 |
| PH$_3$                    | 2.9 | 3.6 | 5.0 | 3.7 | 6.0 | 3.7 |
| H$_2$S                    | 2.2 | 2.6 | 3.6 | 2.8 | 4.3 | 2.8 |
| HCl                       | 1.3 | 1.5 | 2.0 | 1.6 | 2.3 | 1.6 |
| Na$_2$                    | 24.8| 40.2| 48.9| 34.0| 70.4| 35.4|
| Si$_2$                    | 9.2 | 13.8| 18.4| 14.6| 26.1| 19.1|
| P$_2$                     | 7.1 | 6.3 | 13.1| 6.2 | 16.7| 6.2 |
| S$_2$                     | 4.6 | 5.5 | 8.4 | 4.8 | 15.6| 4.7 |
| Cl$_2$                    | 2.8 | 3.3 | 4.7 | 3.2 | 5.7 | 3.2 |
| NaCl                      | 2.2 | 2.9 | 4.5 | 4.0 | 6.0 | 4.4 |
| SiO                       | 3.2 | 3.7 | 6.0 | 3.9 | 7.7 | 4.0 |
| CS                        | 3.5 | 3.4 | 6.4 | 3.6 | 8.1 | 3.6 |
| SO                        | 2.3 | 2.8 | 4.1 | 2.7 | 7.0 | 2.7 |
| ClO                       | 1.7 | 2.0 | 3.5 | 2.3 | 4.5 | 2.3 |
| CIF                       | 1.5 | 1.8 | 2.6 | 1.9 | 3.2 | 1.9 |
| Compound          | Value 1 | Value 2 | Value 3 | Value 4 | Value 5 | Value 6 | Value 7 |
|-------------------|---------|---------|---------|---------|---------|---------|---------|
| Si₂H₆             | 6.3     | 7.8     | 11.4    | 8.5     | 14.2    | 8.9     |         |
| CH₃Cl             | 2.9     | 3.4     | 4.6     | 3.6     | 5.4     | 3.6     | 5.3     |
| H₃COSH            | 3.9     | 4.5     | 6.4     | 4.8     | 7.6     | 4.8     |         |
| HOCl              | 2.0     | 2.5     | 3.4     | 2.5     | 4.2     | 2.5     |         |
| SO₂               | 3.1     | 3.2     | 6.1     | 3.4     | 7.9     | 3.5     | 3.7     |
| BF₃               | 1.4     | 1.7     | 2.4     | 2.0     | 3.0     | 2.2     | 3.3     |
| BCl₃              | 5.7     | 6.2     | 9.9     | 7.0     | 12.2    | 7.2     | 9.4     |
| AlF₃              | 1.6     | 2.0     | 3.0     | 2.6     | 3.8     | 2.9     |         |
| AlCl₃             | 6.0     | 6.9     | 10.7    | 8.0     | 13.1    | 8.3     |         |
| CF₄               | 1.8     | 2.1     | 3.0     | 2.5     | 3.6     | 2.6     | 3.8     |
| CCl₄              | 7.6     | 8.4     | 13.4    | 9.1     | 16.5    | 9.4     | 11.2    |
| COS               | 4.1     | 4.0     | 7.7     | 4.2     | 9.7     | 4.3     |         |
| CS₂               | 7.4     | 6.9     | 14.7    | 7.0     | 19.2    | 7.0     | 8.7     |
| COF₂              | 1.8     | 2.1     | 3.3     | 2.4     | 4.0     | 2.5     |         |
| SiF₄              | 1.9     | 2.3     | 3.4     | 2.9     | 4.2     | 3.1     | 5.5     |
| SiCl₄             | 7.9     | 8.7     | 13.9    | 9.9     | 17.0    | 10.2    |         |
| N₂O               | 2.5     | 2.4     | 4.8     | 2.5     | 6.1     | 2.6     | 3.0     |
| C₂Cl₄             | 8.8     | 10.0    | 16.1    | 10.8    | 20.2    | 11.1    |         |
| CF₃CN             | 3.5     | 3.8     | 6.1     | 4.3     | 7.6     | 4.5     |         |
| CH₃CCH(propyne)   | 4.1     | 4.6     | 6.9     | 4.9     | 8.4     | 5.0     | 6.2     |
| CH₂CCH₂(allene)   | 4.6     | 5.6     | 8.0     | 5.6     | 9.9     | 5.6     |         |
| C₃H₄(cyclopropyne)| 4.3     | 4.8     | 7.0     | 4.9     | 8.4     | 5.0     | 6.2     |
| CH₃CHCH₂(propene) | 4.7     | 5.5     | 7.7     | 5.7     | 9.3     | 5.8     |         |
| C₂H₆              | 4.4     | 5.0     | 7.1     | 5.3     | 8.3     | 5.4     |         |
| C₃H₈(propane)     | 4.7     | 5.5     | 7.5     | 5.8     | 8.9     | 6.0     | 6.3     |
| CH₂CHCHCH₂(butidene)| 6.6   | 8.0     | 11.9    | 8.0     | 15.1    | 8.1     |         |
| C₄H₆(butene)      | 5.6     | 6.5     | 9.6     | 7.0     | 11.7    | 7.2     |         |
| C₄H₆(methylenecyclopropane)| 5.9 | 7.0     | 10.0    | 7.2     | 12.1    | 7.3     |         |
| C₄H₆(bicyclobutane)| 5.7    | 6.2     | 9.3     | 6.5     | 11.0    | 6.7     |         |
| C₄H₆(cyclobutene) | 5.8     | 6.5     | 9.6     | 6.8     | 11.6    | 6.9     |         |
| C₄H₈(Cyclobutane) | 5.8     | 6.6     | 9.3     | 7.0     | 11.0    | 7.2     |         |
| C₄H₈(isobutene)   | 6.2     | 7.2     | 10.4    | 7.6     | 12.5    | 7.8     |         |
| C₄H₁₀(butane)     | 6.2     | 7.2     | 10.0    | 7.7     | 11.8    | 7.9     | 8.2     |
| C₄H₁₀(isobutane)  | 6.2     | 7.2     | 10.1    | 7.7     | 12.0    | 7.9     | 8.1     |
| C₅H₈(spiropentane)| 7.1     | 8.1     | 11.7    | 8.5     | 13.9    | 8.8     |         |
| C₆H₆(benzene)     | 9.4     | 9.6     | 15.6    | 9.8     | 18.9    | 9.9     | 10.0    |
| CH₂F₂(difluromethylene)| 1.6 | 2.0     | 2.7     | 2.3     | 3.3     | 2.4     |         |
| CHF₃(trifluoromethane)| 1.7   | 2.1     | 2.9     | 2.4     | 3.5     | 2.5     | 3.5     |
| CH₂Cl₂(dichloromethane)| 4.3 | 5.0     | 7.2     | 5.3     | 8.7     | 5.5     | 6.5     |
| CHCl₃(chloroform) | 5.9     | 6.7     | 10.2    | 7.2     | 12.5    | 7.5     | 9.5     |
| CH₃NH₂(methylamine)| 2.7     | 3.2     | 4.3     | 3.5     | 5.1     | 3.6     |         |
| CH₃CN(methylcyanide)| 3.4     | 3.8     | 5.7     | 4.0     | 6.9     | 4.1     |         |
| CH₃NO₂(nitromethane)| 3.7     | 4.2     | 6.9     | 4.5     | 8.7     | 4.6     | 7.4     |
| CH₃ONO(methylnitrite)| 3.6     | 4.0     | 6.7     | 4.5     | 8.5     | 4.7     |         |
| CH₃SiH₃(methylsilane)| 4.5     | 5.5     | 7.6     | 5.9     | 9.3     | 6.2     |         |
| CHOOH(formic acid)| 2.3     | 2.6     | 4.1     | 3.0     | 5.2     | 3.2     | 3.4     |
| Compound | 298 K | 300 K | 303 K | 305 K | 307 K | 310 K |
|----------|------|------|------|------|------|------|
| HCOOCH₃ (methyl formate) | 3.7 | 4.3 | 6.4 | 4.7 | 7.8 | 4.9 | 5.0 |
| CH₃CONH₂ (acetamide) | 4.2 | 4.9 | 7.4 | 5.5 | 9.2 | 5.8 | 5.7 |
| C₂H₄NH (aziridine) | 3.9 | 4.4 | 6.3 | 4.7 | 7.5 | 4.8 | 2.6 |
| CN CN (cyanogen) | 4.1 | 4.2 | 8.0 | 4.4 | 10.4 | 4.5 | 4.5 |
| (CH₃)₂NH (dimethylamine) | 4.2 | 5.0 | 6.9 | 5.4 | 8.3 | 5.7 |
| CH₃CH₂NH₂ (trans ethyalmine) | 4.2 | 5.0 | 7.0 | 5.5 | 8.4 | 5.7 |
| CH₂CO (ketene) | 3.2 | 3.6 | 5.8 | 3.8 | 7.1 | 3.9 |
| C₃H₆O (oxirane) | 3.2 | 3.7 | 5.3 | 4.0 | 6.4 | 4.1 |
| CH₃CHO (acetaldehyde) | 3.3 | 3.9 | 5.7 | 4.3 | 7.0 | 4.5 |
| CH₃CH₂OH (ethanol) | 3.6 | 4.3 | 5.9 | 4.7 | 7.0 | 4.8 |
| (CH₃)₂O (dimethylether) | 3.6 | 4.3 | 5.9 | 4.7 | 7.1 | 4.9 |
| C₂H₄S (thioxirane) | 5.5 | 5.9 | 8.0 | 5.4 | 10.4 | 5.7 |
| CH₂CH₂Cl (ethyl chloride) | 6.0 | 7.0 | 9.9 | 7.5 | 11.8 | 7.7 |
| CH₂CH₂OH (isopropanol) | 5.1 | 5.8 | 9.0 | 5.9 | 11.4 | 6.0 |
| (CH₃)₂CO (acetone) | 4.8 | 5.5 | 8.1 | 6.0 | 9.9 | 6.3 | 6.3 |
| CH₃COOH (acetic acid) | 3.7 | 4.3 | 6.4 | 4.7 | 7.8 | 5.0 | 5.1 |
| CH₃COF (acetyl fluoride) | 3.2 | 3.7 | 5.5 | 4.1 | 6.8 | 4.3 |
| CH₃COCI (acetyl chloride) | 4.9 | 5.5 | 8.7 | 6.0 | 10.8 | 6.2 |
| CH₃CH₂CH₂Cl (propyl chloride) | 6.0 | 7.0 | 9.9 | 7.5 | 11.8 | 7.7 |
| (CH₃)₂CHOH (isopropanol) | 5.1 | 6.0 | 8.5 | 6.5 | 10.2 | 6.8 |
| CH₃CH₂OCH₃ (methyl ethylether) | 5.0 | 6.0 | 8.3 | 6.6 | 10.0 | 6.8 |
| (CH₃)₃N (trimethylamine) | 5.8 | 6.7 | 9.7 | 7.4 | 11.8 | 7.8 |
| C₄H₆O (furan) | 6.2 | 6.6 | 10.5 | 6.8 | 12.7 | 7.0 |
| C₄H₄S (thiophene) | 8.6 | 8.7 | 14.8 | 9.0 | 18.1 | 9.1 | 9.7 |
| C₄H₆NH (pyrole) | 7.0 | 7.4 | 11.6 | 7.7 | 14.0 | 7.8 |
| C₅H₅N (pyridine) | 8.6 | 8.7 | 14.5 | 9.1 | 17.6 | 9.2 | 9.5 |
| CCH (ethynyl radical) | 2.7 | 3.3 | 4.9 | 3.6 | 5.9 | 3.7 |
| CH₃CO | 3.1 | 3.8 | 5.6 | 4.2 | 6.6 | 4.5 |
| CH₂OH (hydroxymethyl) | 1.9 | 2.4 | 3.3 | 2.8 | 4.1 | 2.9 |
| CINO | 3.9 | 4.4 | 8.7 | 4.3 | 12.6 | 4.4 |
| NF₃ | 1.8 | 2.2 | 3.3 | 2.4 | 4.3 | 2.5 | 3.6 |
| PF₃ | 2.5 | 3.0 | 4.6 | 3.4 | 5.8 | 3.6 |
| O₃ | 2.5 | 2.7 | 5.5 | 2.4 | 7.8 | 2.4 | 3.2 |
| F₂O | 1.4 | 1.8 | 2.6 | 1.8 | 3.4 | 1.8 |
| ClF₃ | 3.0 | 3.7 | 6.4 | 3.8 | 8.8 | 3.9 | 6.3 |
| C₇F₄ | 3.0 | 3.5 | 5.4 | 3.9 | 6.9 | 4.1 |
| CH₃O (methoxy radical) | 1.9 | 2.4 | 3.3 | 2.7 | 4.2 | 2.9 |
| CH₃CH₂O | 3.4 | 4.1 | 5.8 | 4.6 | 7.3 | 4.8 |
| CH₃S (methylsulfide radical) | 3.3 | 4.0 | 5.5 | 4.3 | 6.7 | 4.4 |
| CH₃CH₂ (ethyl radical) | 2.9 | 3.5 | 4.7 | 3.9 | 5.6 | 4.0 |
As mentioned earlier, empirical schemes that convert the SOS polarizabilities to screened polarizabilities have been devised and applied to carbon fullerenes \[13, 14, 16, 31\]. These schemes were usually obtained in the random phase approximation and were applied to spherical molecules like fullerenes and cylindrical systems like nanotubes. Their application to molecules with arbitrary geometry has not yet been reported. An alternative possibility to improve upon the SOS polarizability will be to improve the approximation for the exchange-correlation functional. Correcting for the self-interaction in the approximate functional may improve the SOS polarizabilities. It has been found that the self-interaction corrections (SIC) significantly improves the eigenvalues and the band gap \[32\]. The SIC implementation is however quite complicated to implement and computationally expensive \[33\]. The time dependent DFT (TD-DFT) within the linear response regime is another popular method for obtaining excitation energies but like the finite-field method it breaks the point-group symmetry. Much simpler approach would be to assume that the orbitals or the transition dipole moments obtained in the approximate DFT models to be reasonably accurate and correct only the eigenvalues using simple schemes.

There are a number of methods in the literature that try to improve upon the HOMO-LUMO energy gap in the approximate DFT models typically by correcting the eigenvalues of the single-particle equations. Such corrections should result in some improvements in the SOS polarizability. Most of these methods are, however, quite complex and computationally expensive, limiting their advantages for correcting $\alpha_{SOS}$ over the finite field method in terms of computational time. Hence simple schemes for correcting the eigenvalues are more appealing \[34, 35, 36\] and worth exploring in calculation of $\alpha_{SOS}$. Such simple schemes have been used in calculations of photoelectron spectra with some success \[37\]. The simplest such a correction would be to replace the $\Delta_{HL}$ by the quasiparticle gap. The latter set of quantities can be computed by finite difference method or the so called $\Delta SCF$ method. This requires two additional self-consistent calculations, one for cation and other for anion. The correction $\delta$ to the $\Delta_{HL}$ is then $E(N - 1) + E(N + 1) - 2E(N) - \epsilon_{HOMO} + \epsilon_{LUMO}$, where, $E(N)$ is the self-consistent total energy of the system containing $N$ electrons, $\epsilon_{HOMO/LUMO}$ are the eigenvalues of the HOMO/LUMO of the neutral molecule. This correction, when applied to all single particle energies, would shift the occupied and unoccupied eigenvalues in opposite directions and hence may be useful in getting better estimate of $\alpha_{SOS}$. Its application to the $Li_2$ for which the difference between the $\alpha_{FF}$ and $\alpha_{SOS}$ is large, indicate that this correction
overcorrects $\alpha_{SOS}$, roughly by a factor of two (from 57.0 Å$^3$ to 19.0 Å$^3$ for PBE).

Another possible scheme can be devised by noting that the HF overestimates the $\alpha_{SOS}$ whereas the PBE underestimates. It is possible to mix the HF $\alpha_{SOS}$ and the PBE $\alpha_{SOS}$ to obtain finite-field quality polarizability. In absence of more accurate data, we choose B3LYP finite-field polarizabilities as a target set. The following interpolation scheme can be used:

$$\alpha^{\text{mix}} = (1 - x) \cdot \alpha_{HF}^{SOS} + x \cdot \alpha_{PBE}^{SOS},$$

where the parameter $x$ ($0 < x < 1$) can be determined by minimizing the mean absolute error (MAE) in the $\alpha^{\text{mix}}$ and $\alpha_{FF}^{B3LYP}$. The minimization procedure gives the optimal mixing parameter to be 0.22. The MAE at the minimum is 0.4 Å$^3$. Thus about 80% of HF $\alpha_{SOS}$ mixed with about 20% of the PBE $\alpha_{SOS}$ will give $\alpha_{SOS}$ comparable to the B3LYP $\alpha_{FF}$. In this application more HF than DFT is required, whereas Becke needed less HF than DFT for optimizing B3LYP for atomization energies[1]. This procedure requires calculation of $\alpha_{SOS}$ in two models which could be performed efficiently by making use of any symmetry that system may possess. Thus it could be applied to symmetric quantum dots, fullerenes and nanocrystals to obtain estimates of polarizability.

We note that similar idea was explored for a few molecules by Dunlap and Karna[38]. These authors used average values of eigenvalues in the HF and the local-density approximation (DFT) eigenvalues in the SOS expression (Eq. 4).

In conclusion, a systematic comparison of the SOS and FF methods for the calculation of molecular dipole polarizability for a set of 142 molecules from the extended G2 set has been performed. The trends in the two sets, $\alpha_{SOS}$ and $\alpha_{FF}$, of polarizabilities are examined in three widely used single-particle methods: The HF approximation, the PBE-GGA within DFT, and the hybrid B3LYP model that mixes DFT exchange with HF exchange. In order to minimize the other sources that can lead to differences in the polarizabilities in different models, the same set of molecular geometries (optimized at the B3LYP/6-311G** level) and 6-311++G(d,p) orbital basis set was used. The calculations show that $\alpha_{SOS}$ polarizabilities are almost always underestimated in the HF method. However, exceptions to the trend do exist. The $\alpha_{SOS}$ of P$_2$, CS, COS, and N$_2$O are overestimated with respect to the $\alpha_{FF}$ polarizability. On the other hand, in the PBE-GGA model, $\alpha_{SOS}$ is always overestimated with respect to the $\alpha_{FF}$. These observations correlate with the generally observed trend of the respective underestimation and overestimation of the HOMO-LUMO gap in the PBE-GGA and HF models. Although the $\alpha_{SOS}$ overestimates the $\alpha_{FF}$ in the hybrid B3LYP, the differences in the two polarizabilities is less than that observed for the PBE model.
The comparison of screened polarizabilities $\alpha_{FF}$ in the three models shows that the $\alpha_{FF}$ in B3LYP and PBE models are larger than those calculated with the HF method. Thus inclusion of correlation effects, in general, leads to increase in (finite-field) polarizability. Finally, a simple scheme that interpolates $\alpha_{SOS}$ values in HF and PBE to obtain B3LYP $\alpha_{FF}$ is devised by minimizing the mean absolute error. A simple scheme like this may be useful to estimate polarizabilities of large symmetric molecules such as fullerenes, quantum dots or nanocrystalline materials.

Authors acknowledge Dr. S. P. Karna and Prof. P. B. Allen for discussions. The Gaussian03 calculations were performed at the Army Research Laboratory Major Shared Resource Center (ARL-MSRC). This work was supported in part by the Office of Naval Research, directly and through the Naval Research Laboratory (ONR Grant No. N000140211046, and 05PR07548-00) and in parts by the NSF through CREST grant (Grant No. NIRT-0304122), by the University of Texas at El Paso.

[1] A. D. Becke, J. Chem. Phys. 98, 5648 (1993);  
[2] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B 37, 785 (1988); B. Miehlich, A. Savin, H. Stoll, and H. Preuss, Chem. Phys. Lett. 157, 200 (1989).  
[3] J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. 77, 3865(1996).  
[4] G. D. Mahan and K. R. Subbaswamy, Local Density Theory of polarizability, Plenum Press, New York (1990); D. M. Bishop, Rev. Mod. Phys. bf 62, 343 (1990); Electric-Dipole Polarizabilities of Atoms, Molecules and Clusters, K.D. Bonin and V.V. Kresin (World Scientific, 1997).  
[5] For a recent review of this topic, see for example Theoretical and Computational Modelling of NLO and Electronic Materials, edited by S.P. Karna and A.T. Yeats (ACS Press, Washington, DC, 1996).  
[6] G. D. Mahan, Phys. Rev. A 22, 1780 (1980).  
[7] H. D. Cohen and C. C. J. Roothan, J. Chem. Phys. 43, S34 (1965); J. A. Pople, J. W. McIver Jr., and N. S. Ostlund, J. Chem. Phys. 49, 2960 (1968); A. D. Buckingham, Adv. Chem. Phys. 12, 107 (1967); H. A. Kurtz, J. J. P. Stewart, and K. Dieter, J. Comp. Chem. 11, 82 (1990). H. A. Kurtz, I. J. Quant. Chem. S24, 791 (1990); A. A. Quong and M. R. Pederson,
Phys. Rev. B 46, 12906 (1992); J. Guan, M. E. Casida, A. M. Köster, and D. R. Salahub, Phys. Rev. B 52, 2184 (1995); S. A. Blundell, C. Guet, and R. R. Zope, Phys. Rev. Lett. 84, 4826 (2000).

[8] C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. (London) A 191, 39 (1947); H. Peng, Proc. Roy. Soc. (London), A 178, 499 (1941); L. C. Allen, Phys. Rev. 118, 167 (1960); A. Dalgarno, Adv. Phys. 11, 281 (1962).

[9] J. Gerratt and I. M. Mills, J. Chem. Phys. 49, 1719 (1968); R. McWeeny, Rev. Mod. Phys. 32, 335 (1960); R. McWeeny, Phys. Rev. 128, 1028 (1961); R. M. Stevens, R. M. Pitzer, and W. N. Lipscomb, J. Chem. Phys. 38, 550 (1963); J. L. Dodds, R. McWeeny, W. T. Raynes, and J. P. Riley, Mol. Phys. 33, 611 (1977); J. L. Dodds, R. McWeeny, and A. J. Sadlej, Mol. Phys. 34, 1779 (1977); Y. Osamura, Y. Yamaguchi, and H. F. Schaefer III, J. Chem. Phys. 77, 383 (1982); P. Pulay, J. Chem. Phys. 78, 5043 (1983); C. E. Dykstra and P. G. Jasiens, Chem. Phys. Lett. 109, 388 (1984).

[10] M. J. Stott and E. Zaremba, Phys. Rev. A 21, 12 (1980); Erratum: 22, 2293 (1980).

[11] M. R. Pederson and A. A. Quong, Phys. Rev. B 46, 13584 (1992).

[12] A. Szabo and N. S. Ostlund, Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory, 1st ed., McGraw-Hill, New York, 1989.

[13] G. F. Bertsch, A. Bulgac, D. Tománek, and Y. Wang, Phys. Rev. Lett. 67, 2690 (1991).

[14] L. X. Benedict, S. G. Louie, and M. L. Cohen, Phys. Rev. B 52, 8541 (1995).

[15] F. Alasia, R. A. Broglia, H. E. Roman, L. L. Serra, G. Colo, anf J. M. Pacheco, J. Phys. B 27, L643 (1994).

[16] E. Westin, A. Rosen, G Te Velde and E. J. Baerends, J. Phys. B 29, 5087 (1996).

[17] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[18] T. Koopmans, Physica (Utrecht) 1, 104 (1933).

[19] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Jr. Phys. Rev. Lett. 49, 1691 (1982); M. Levy, J. P. Perdew and V. Sahni, Phys. Rev. A 30, 2745 (1984); C. O. Almbladh and U. von Barth, Phys. Rev. B 31, 3231 (1985); L. Kleinman Phys. Rev. B 56, 16029 (1997); J. P. Perdew and M. Levy, Phys. Rev. B 56, 16021 (1997); L. Kleinman, Phys. Rev. B 56, 12042 (1997); M. E. Casida, Phys. Rev. B 59, 4694 (1999); M. K. Harbola, Phys. Rev. B 60, 4545 (1999).
[20] J. F. Janak, Phys. Rev. B 18, 7165 (1978).
[21] R. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. B 37, 10159 (1988).
[22] A. Fleszar, Phys. Rev. B 64, 245204 (2001).
[23] J. P. Perdew and M. Levy, Phys. Rev. Lett. 51, 1884 (1983); L. J. Sham and M. Schlüter, ibid 51, 1888 (1983).
[24] R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. 61, 689 (1989).
[25] R. R. Zope and B. I. Dunlap, Chem. Phys. Lett. 422, 451 (2006); Y. Zhao, Y.-H. Kim, M.-H. Du, and S. B. Zhang, Phys. Rev. Lett. 93, 015502 (2004).
[26] A. D. McLean and G. S. Chandler, J. Chem. Phys. 72, 5639 (1980); R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, J. Chem. Phys. 72, 650 (1980)

Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskor, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
[28] M. R. Pederson and K. A. Jackson, Phys. Rev. B. 41, 7453 (1990); ibid 43, 7312 (1991); K. A. Jackson and M. R. Pederson, ibid 42, 3276 (1990).
[29] M. R. Pederson and T. Baruah, Lecture series in Computer and Computational Sciences, 3 156 (2005).
[30] C. R. C. Handbook of Chemistry and Physics, 85th edition, (2004-2005).
[31] G. K. Gueorguiev, J. J. Pacheco, and D. Tománek, Phys. Rev. Lett. 92, 215501 (2004).
[32] J. P. Perdew in Advances in Quantum Chemistry, ed. S. B. Trickey, Vol. 21, (1990).
[33] M. R. Pederson, R. A. Heaton and C. C. Lin, J. Chem. Phys. 82, 2688 (1985).
[34] P. H. Acioli and J. Jellinek, J. Chem. Phys. 118, 7783 (2003). D. P. Chong, O. V. Gritsenko, E. J. Baerends, J. Chem. Phys. 116 1760 (2002).

[35] S. B. Trickey, Phys. Rev. Lett. 56, 881 (1986).

[36] M. Harris and P. Ballone, Chem. Phys. Lett. 303, 420 (1999).

[37] Gengeliczki, Z; Pongor, CI; Sztaray, B Organometallics, 25 2553 (2006); Walter, M; Hakkinen, H E. Phys. J. D, 33 393 (2005); Moseler, M; Huber, B; Hakkinen, H; et al. Phys. Rev. B. 68 165413 (2003); Acioli, PH; Jellinek, J Phys. Rev. Lett. 89 213402 (2002).

[38] B. I. Dunlap and S. P. Karna, Nonlinear Optical Materials, Eds. S. P. Karna and A. T. Yates, ACS Symposium Series, 628, 164 (1996).