

Understanding and correcting the self-interaction error in the electrical response of hydrogen chains

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Semilocal density functionals such as the local-spin-density and generalized-gradient approximations are known to overestimate the polarizabilities and especially the hyperpolarizabilities of long-chain molecules, the latter by as much as a factor of 10 or more in model hydrogen chains. These quantities are much better predicted by exact-exchange methods such as Hartree-Fock or optimized effective potential. We show here that the semilocal functionals, after full or scaled-down Perdew-Zunger self-interaction correction (SIC), are about as good as the exact-exchange methods for these quantities. As is the case for the exact-exchange methods, SIC is fully nonlocal and exact for all one-electron densities, and (more relevantly to the electrical response) tends to maintain an integer number of electrons on each H_2 chain unit to a greater extent than the semilocal functionals do. In this study, the SIC energy is minimized directly, without an optimized effective potential.

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First-principles density-functional methods [1,2] play an important role in the description of the electronic structure of molecules, clusters, and solids. The accuracy of the density-functional calculations relies on the approximation to the exchange-correlation energy. Semilocal density functionals such as the local-spin-density (LSD) approximation [2] and the generalized-gradient approximation (GGA) [3] often predict good-quality ground-state properties near equilibrium geometries, but predictions of the linear [4–10] and nonlinear [4–6] electrical response of molecular chains, and other problems that involve fractional numbers of electrons [11,12], have remained a challenge.

The overestimation of the static polarizability and hyperpolarizability by LSD and GGA has been known for a long time. It arises from the underestimated or wrongly signed [4,8] counteraction [5] to an applied external field in the semilocal exchange-correlation potentials. When a static electric field is applied to a chain of atoms, charge transfer occurs along the backbone of the chain. This induced polarization is a nonlocal effect, requiring a nonlocal dependence of the exchange-correlation energy on the density or orbitals. The local and semilocal approximations fail to provide the correct counteracting response field that reduces the electrical response.

The needed nonlocal effects are properly described by highly accurate wave-function methods (Møller-Plesset and coupled-cluster), and even Hartree-Fock (HF) theory without correlation can provide a good starting point for these sophisticated wave-function techniques. The Hartree-Fock method includes some nonlocal effects, and the exact nonlocal exchange itself largely corrects the tremendous overestimation of the nonlinear response in the semi-local approaches (Fig. 1). The exact-exchange (EXX) or optimized effective potential (OEP) [13–20] density-functional theory (DFT) exhibits functional nonlocality as well, although it is associated with a local multiplicative potential. It can provide Hartree-Fock-level results and can be chosen as an al-

ternative thereto. Approximations to the EXX or OEP for exchange, such as the Krieger-Li-Iafrate (KLI) [21] and common-energy-denominator-approximation (CEDA) methods [22], yield hyperpolarizabilities that are better than those of the semilocal functionals but less accurate than those of the EXX method [5].

The failure of the semilocal approaches such as LSD and GGA for the electric response seems rooted in the self-interaction error inherent to these approximations and largely absent from exact-exchange methods. This was demonstrated by calculations of the polarizability in Refs. [8,9], and will be demonstrated here more dramatically by calculations of the hyperpolarizability. The one-electron self-interaction error is the error for one-electron densities, while many-electron self-interaction error (a concept that was developed recently) is an incorrect behavior of the energy of an open system as a function of the average number of electrons in it [23–25]. Both errors of semilocal functionals are corrected

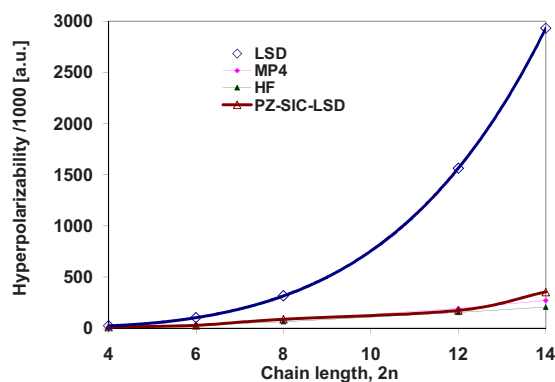


FIG. 1. (Color online) Hyperpolarizability (in 10^{-3} a.u.) vs chain length n for hydrogen chains H_{2n} . If there were no interaction and no charge transfer between H_2 chain units, then the energy, polarizability, and hyperpolarizability would all be proportional to the number of such units, n .

by the method of Perdew and Zunger [26], the former exactly and the latter approximately. Self-interaction correction (SIC) is greater to the extent that the average electron number differs from an integer. SIC tends to force an integer number of electrons onto a separated open system [23], and in this way can provide a needed field counteraction that limits the electrical response of a chain of nearly separated units. In simpler language, SIC makes the electrons “stick tighter” to the chain units, reducing the charge transfer that overestimates the electrical response when semilocal functionals are used. In more advanced language, SIC mimics [11,12] the derivative discontinuity [27] of the exact exchange-correlation energy for a separated open system, and the residue of this derivative discontinuity for a chain unit provides the needed field counteraction [6]. The success of SIC for the electrical response must be a consequence of SIC’s approximate many-electron self-interaction freedom, and not only of its one-electron self-interaction freedom: In an exact treatment, there is no field counteraction for a one-electron ground state, where the “response” part of the exchange-correlation potential vanishes, and none from exchange in a two-electron system [5].

The self-interaction error was evident long ago within LSD, and led Perdew and Zunger (PZ) [26] to propose a self-interaction correction to LSD or other density-functional approximations. A recently developed scaled-down version of the PZ-SIC [28] has one-electron self-interaction freedom like PZ-SIC, with a better description of equilibrium properties of molecules but less many-electron self-interaction freedom [23]. Both the PZ-SIC and its scaled-down versions are orbital-by-orbital corrections of the SI error and have the form

$$E_{xc}^{SIC}[\{\rho_n^\sigma\}] = E_{xc}^{\text{approx}}[\rho^\uparrow, \rho^\downarrow] - \sum_{n\sigma}^{\text{occupied}} \gamma_{n\sigma} (U[\rho_n^\sigma] + E_{xc}^{\text{approx}}[\rho_n^\sigma, 0]), \quad (1)$$

where $\rho_n^\sigma = |\psi_{n\sigma}|^2$, $\rho^\sigma = \sum_n^{\text{occup}} \rho_n^\sigma$, and

$$\gamma_{n\sigma} = \int d^3r (\tau_\sigma^w / \tau_\sigma)^k \rho_n^\sigma. \quad (2)$$

Here U , the Hartree electrostatic energy, provides full non-locality. τ_σ^w is the Weizsäcker kinetic energy density and τ_σ is the positive kinetic energy density of σ -spin electrons. The scale-down factor $\gamma_{n\sigma}$ is 1 for ground states with two or fewer electrons (where PZ-SIC is exact for exchange) [23,24], but lies between 0 and 1 for many-electron densities. The scaled-down SIC has only one adjustable parameter k that can fine-tune the scale-down factor in a many-electron region between 0 and 1. $k=0$ is the original PZ-SIC, with $\gamma_{n\sigma}=1$ and thus with exact self-exchange for the SIC orbitals. For the scaled-down SIC, we chose $k=1$ and 2 as typical (but not necessarily optimal) values.

The SIC energy of Eq. (1) depends on the occupied orbitals, and (unlike the case for Hartree-Fock theory) is not invariant under unitary transformation of them [26]. The orthonormal occupied orbitals that minimize the energy are typically localized, and guarantee self-consistency and size

TABLE I. Longitudinal polarizabilities α with semilocal and self-interaction-corrected density functionals for hydrogen chains of increasing length. The MP4 and CCSD(T) values are the standard of accuracy. The 6-311++G(d,p) basis set was used in all calculations except where noted. The MP4-acT calculations employ a larger aug-cc-pVTZ basis set. All values are in atomic units.

Method	H ₄	H ₆	H ₈	H ₁₂	H ₁₄
LSD	37.6	72.9	115.3	212.1	263
PBE	36.0	69.3	108.7	197.5	244
HF	32.2	56.6	83.0	138.6	167
MP4	29.5	51.9	76.2	127.3	155
MP4-acT	30.1	53.1	78.2		
CCSD(T)	29.0	50.9	74.4	124.0	
PZ-SIC-LSD ^a	33.0	59.7	89.1	152.0	184
PZ-SIC-PBE ^a	33.7	60.8	87.2	155.9	189
$k=1$ SIC-LSD ^a	32.6	58.6	87.2	148.3	180
$k=2$ SIC-PBE ^a	34.0	62.6	94.8	164.6	200
LSD ^b	37.6	72.7	114.6	210.5	
xKLI ^b	33.1	60.2	90.6	156.3	
xOEP ^b	32.2	56.6	84.2	138.1	

^aThe DFT calculations use grid=120770.

^bReference [5].

consistency [26]. We follow the method of Ref. [29], in which the SIC energy is minimized via a gradient search with Löwdin orthogonalization. Other methods for solving the SIC equations may impose additional constraints. The canonical delocalized orbitals that are unitarily equivalent to the SIC orbitals can be constrained to belong to a common effective potential that is either nonlocal [30,31] or local [8,9]. These constraints raise the energy, but typically not by much. The advantage of a local or Kohn-Sham potential is that it can be plotted to show the field-counteracting term [8]. But a disadvantage is that the complicated full OEP [6,7,14–20,9] formalism should ideally be employed, since the simpler KLI and CEDA formalisms do not achieve full self-consistency (at least for the hyperpolarizabilities in exact-exchange approximations). We have learned of recent KLI- [8] and OEP- [9] SIC calculations for the polarizabilities of the hydrogen chains, but ours may be the first SIC calculation for the hyperpolarizabilities of the chains.

The linear hydrogen chains (with the structure described below) usefully model the response properties of the more complicated polymers such as polyacetylenes, and have proven a challenging test for density functionals [4,6,32]. The linear hydrogen chains we selected have alternating bond lengths with interatomic distances of 2 and 3 bohrs [4,6]. These interatomic distances are beyond the covalent bond length, so the system is only weakly connected and has identifiable fragments (the H₂ chain units) with fractional charges, leading to substantial self-interaction errors of semilocal functionals. We compute the polarizability and second hyperpolarizability for hydrogen chains with increasing chain length, reporting our results in Tables I and II.

The polarizabilities and second hyperpolarizabilities are computed as the derivatives of the dipole moment μ or en-

TABLE II. Same as Table I but for the longitudinal second hyperpolarizabilities χ . Here $\chi/10^3$ is displayed.

Method	H ₄	H ₆	H ₈	H ₁₂	H ₁₄
LSD	23	102	315	1500	2900
PBE	21	100	289	1300	2400
HF	9	31	63	154	206
MP4	13	35	76	193	271
MP4-acT	10	37	78		
CCSD(T)	10	34	72	176	
PZ-SIC-LSD ^a	9	31	88	177	325
PZ-SIC-PBE ^a	4	44	78	149	187
$k=1$ SIC-LSD ^a	7	33	88	187	172
$k=2$ SIC-PBE ^a	9	34	83	193	260
LSD ^b	23	101	280	1200	
xKLI ^b	10	36	90	300	
xOEP ^b	9	30	68	144	

^aThe DFT calculations use grid=120770.

^bReference [5].

ergy E with respect to the applied longitudinal electric field F : $\alpha = \partial\mu / \partial F$ and $\chi = \partial^3\mu / \partial^3 F$, from the Taylor expansion of the energy or dipole moment of the molecule in the presence of an electric field F : $\mu(F) = \alpha F + \chi F^3/6$, and

$$E(F) = E(0) - \alpha F^2/2 - \chi F^4/24 \quad (3)$$

for a molecule with inversion symmetry in zero field ($F=0$). By the Hellmann-Feynman theorem, the derivative of the ground-state energy is the same as the dipole moment: $dE/dF = -\mu(F)$. In a precise calculation, the dipole expressions stemming from the energy and from the integral of the total charge density become equal. But numerically this could require a huge grid and basis set. Equal convergence cannot be assured for both energy and charge. The energy has a second-order error in convergence while the dipole has a first-order one. Thus an inconsistency appears when the dipole moment is taken from the total charge density, and in reported calculations we use only the energy in order to extract the derivatives.

Our approach is to make a least-squares fit of Eq. (3) to calculated energies for evenly spaced fields F in the range $0 < F < F_{\max}$. The maximum F_{\max} of the external electric field requires special care. When F_{\max} is too small, the hyperpolarizability effects are too small to resolve. When F_{\max} is too large, the contributions of higher hyperpolarizabilities cannot be ignored. A proper F_{\max} lies on a plateau over which the extracted polarizability and hyperpolarizability are stable. The width of this plateau could be increased by using polynomials of higher than fourth order in Eq. (3). In this work, we have chosen $F_{\max} = 0.007$ a.u., which makes the hyperpolarizability term in Eq. (3) less than 1% of the polarizability term. For the longer chains treated with semilocal functionals, this F_{\max} may be too large for optimum accuracy. We will investigate this point in future work.

To avoid the contribution of the first-order hyperpolarizability and enhance the numerical accuracy, we used the in-

version symmetry of the hydrogen chains to construct and fit to an even function for the energy versus electric field. This way the odd coefficients disappear for the energy polynomial. A fourth-order polynomial was used in the fitting procedure to the energy. Polarizabilities are computed with good accuracy. The second hyperpolarizability, however, is the fourth-order derivative with respect to the energy, and it shows extreme sensitivity to any change of (or numerical error in) the calculated energy, leading to an uncertainty of as much as $\pm 20\%$ in the computed values.

Basis-set completeness appears to be a factor that strongly influences the nonlinear response properties. It has been shown [32] for hydrocarbons that an adequate basis set to compute accurate response properties is of double-zeta quality with diffuse functions. In this work, a triple-zeta quality basis set with one diffuse function for hydrogen was chosen for the hydrogen chains, as in Ref. [4]. We present the performance of the LSD and PBE-GGA density functionals without and with the PZ-SIC ($k=0$) and scaled-down SIC ($k=1$ or 2) approaches, applying ultrafine and unpruned integration grids respectively. The larger unpruned grid involves 120 radial and 770 angular points per shell in our calculations. As a standard, the fourth-order Møller-Plesset (MP4) polarizabilities and hyperpolarizabilities were computed as well. All calculations were carried out with the developmental version of the Gaussian suite of programs [33] with the 6-311++G(d,p) basis set. The MP4 values change only slightly upon improvement of the basis set to augmented correlation-consistent polarized-valence zeta (aug-cc-pVTZ), or improvement of the electron correlation method to CCSD(T).

Our results are presented in Tables I (polarizability) and II (hyperpolarizability). Regardless of the density functional employed, all SIC methods dramatically improve the hyperpolarizabilities and polarizabilities. The improvement strengthens toward the longer chains.

We believe that PZ-SIC performs like Hartree-Fock theory for the electrical response for the following reason: Each H₂ unit of an H_{2n} chain is a partly isolated open system in which the average electron number deviates from an integer. Over such a system, the exchange-hole density around an electron integrates to the same number in PZ-SIC [26,23] as in Hartree-Fock theory [24]. This number degrades slightly in scaled-down SIC [23], and substantially for semilocal functionals without SIC. Thus the exchange energy (exact in Hartree-Fock theory) of this open system is described well by PZ-SIC, leading to approximate many-electron self-interaction freedom (as defined earlier). But the exchange energy degrades as we move toward the semilocal density functionals.

Partly isolated open systems arising from moderately stretched bonds are found not only in the H_{2n} chains but also in the transition states of chemical reactions. For the energy barriers that arise from the transition states, both PZ and scaled-down SIC work well [28]. So it is not surprising that the same is found here for the electrical response of the H_{2n} chains. For the highly stretched bonds that arise in the dissociation limit [23,34,35], PZ-SIC is superior [23] to scaled-down SIC, while the opposite is true [28,29] for the equilibrium bonds of molecules. Moderately stretched bonds may

represent a crossover point where both versions of SIC work well.

Our numerical results and arguments suggest that an accurate treatment of the hyperpolarizability of stretched hydrogen chains requires at least approximate many-electron self-interaction freedom, as achieved by SIC or exact-exchange methods. Full self-consistency or direct minimization of the energy is apparently also needed, as suggested by the superiority of Hartree-Fock or exchange-only OEP to exchange-only KLI. In separate work [36], we will present a

simple analytic charge-transfer model to further explain the strong nonlinearity and SIC dependence seen, for example, in Fig. 1, and we will refine the numerical accuracy of the hyperpolarizabilities reported here.

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