Variational calculation of polarizability and second hyperpolarizability of two-electron systems

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Application of the perturbation expansion of the variational principle of energy in density-functional theory is demonstrated by calculating the static dipole polarizability α and second hyperpolarizability γ of the two-electron systems H^-, He, and Li^+. Calculations are performed within both Hartree-Fock and density-functional theories. In the approach employed, energy change at each order (second and fourth in our case) is minimized so that no electric field needs to be applied explicitly. This makes the calculation very accurate. Significantly, Hartree-Fock results obtained by us, to our knowledge, are larger (and therefore closer to experiments) than those reported in the literature calculated by the finite field method, and also by other methods. [S1050-2947(96)10406-6]

Response properties of atomic systems are described well by their dipole polarizabilities. At low intensities of the applied electric field atoms respond linearly. That is, their induced dipole moment is proportional to the applied field; the constant of proportionality is the dipole polarizability α (tensor in general). However, the situation is different when the applied field is intense, such as in a laser light. The induced dipole can then have higher-order contributions from the field. These are described by the first and second hyperpolarizability, β and γ, respectively. This gives rise to interesting nonlinear effects such as second- and third-harmonic generation, intensity-dependent refractive index, etc.

Theoretically α, β, and γ are calculated using perturbation theory [1] up to the appropriate order. For example, to obtain α one solves the first-order perturbation equation. However, calculations become more and more complicated for higher orders. A great simplification comes about by the $2n+1$ theorem [1,2]: the $(2n+1)$-order derivative of eigenenergy can be calculated from the wave function and its derivatives up to order n. Thus to calculate γ (fourth-order energy) one requires a wave function only up to order 2. The theorem is easy to prove if the eigenstates are known. In practice, however, the many-electron Schrödinger equation cannot be solved exactly; therefore methods, such as Hartree-Fock [3], based on the variational principle of energy, are employed to obtain approximate solutions of the Schrödinger equation. The applicability of the $2n+1$ theorem to such methods is not obvious. Thus the theorem has been studied and applied [4–8] over the years on a case-by-case basis.

One of the most extensively used methods in recent times to obtain energies and densities of interacting many-electron systems is the density-functional theory (DFT) [9] approach. This approach is also based on the variational principle for the energy and shows that the ground-state energy of a many-electron system can be expressed as a functional $E[\rho]$ of its ground-state density. The density in turn is obtained from the self-consistent solutions of the Kohn-Sham (KS) equation [9]

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \right]\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \quad (1)$$

and is given as

$$\rho(\mathbf{r}) = \sum_{i=\text{occ}} |\phi_i(\mathbf{r})|^2. \quad (2)$$

In Eq. (1) $v_{\text{ext}}(\mathbf{r})$ is the external field. The Hartree potential $v_H(\mathbf{r})$ and the exchange-correlation potential $v_{\text{xc}}(\mathbf{r})$, both of which are local operators, represent the electron-electron interaction. They are the functional derivatives of the corresponding energy functionals with respect to the density. However, the exact exchange-correlation energy functional is not known and therefore some approximate form for it is applied in solving Eq. (1). The most widely used is the local-density approximation (LDA) [9]. Equation (2) can be expanded [10] perturbatively if the external potential is changed by a small amount. As such DFT has also been employed to calculate the polarizabilities [10] and hyperpolarizabilities [8,10–12] of many-electron systems. Thus solutions up to first order give the corresponding change in density and lead to polarizability and the higher-order changes give hyperpolarizabilities. In particular to obtain γ, one has to get [12] density up to the third order $\rho^{(3)}$ and calculate its moment. However, for this one must solve the perturbed Kohn-Sham equation up to order 3. In contrast, if the $2n+1$ theorem could be applied, solutions only up to second order would be sufficient [8]. Can the $2n+1$ theorem be applied in DFT?

Some time ago it was proved [8] that the theorem is indeed valid in DFT, which means that the Kohn-Sham equation needs to be solved only up to order n in perturbation to calculate up to $(2n+1)$-order total-energy changes $E^{(2n+1)}$. This is a result of the nontrivial cancellation [8] of corrections to the orbital eigenenergies, Hartree and exchange-correlation energies, and the corresponding potentials. Based on this, an explicit expression for $E^{(2n+1)}$ can be written [8,13] in terms of orbitals up to $\phi^{(n)}$. Furthermore, it has been proved recently that $E^{(2n)}$ is also variational [2] with respect to $\phi^{(n)}$. By nature of the proof, the statements above are also valid within Hartree-Fock theory for two-electron systems, since the exchange energy for these systems is easily expressed as a functional of the density. In a

nutshell, if the wave function is known *exactly* up to order n, the $(n+1)$-order wave function gives corrections in the energy of the order of $2n+2$ and this energy term is variational with respect to $\phi^{(n+1)}$. In this paper we show that these two facts together can also be employed in a variational manner to calculate polarizabilities and hyperpolarizabilities of an electronic system. Notice that variationally too once the energy up to order $E^{(2n)}$ has been minimized, with wave function up to order n, the next-order correction will give an energy change in $(2n+2)$-order energy.

Starting from a ground-state KS wave function, accurate first-order correction to it can be obtained by minimizing $E^{(2)}$. Once the first-order wave function is known the total energy up to $E^{(3)}$ is also known. Thus $\phi^{(2)}$ can now be obtained variationally by minimizing $E^{(4)}$, and gives energy

up to fifth order. One can thus build up higher and higher derivatives of the wave function and the energy.

In this work we consider the examples of two-electron systems H^-, He, and Li^+ within both Hartree-Fock and Kohn-Sham LDA and calculate their polarizabilities and second hyperpolarizability (β is zero by symmetry) by applying the above-mentioned procedure. For H^-, only Hartree-Fock (HF) results are presented as the LDA solution for it does not converge [14]. Significantly, we show that within HF the values of γ obtained by us are larger than those reported in the literature [15–18] also determined variationally by other methods. The KS results, however, are close to those obtained by solving the complete LDA equation up to order 3.

Expressions for the second- and the fourth-order energy in terms of the Kohn-Sham orbitals (for spherical one-orbital systems considered in this paper) in the presence of the perturbing Hamiltonian $H^{(1)} = r\cos\theta$ are given as [13]

$$E^{(2)} = \langle \phi^{(1)} | H_0 - E_0 | \phi^{(1)} \rangle + \langle \phi^{(1)} | H^1 | \phi^{(0)} \rangle + \langle \phi^{(0)} | H^1 | \phi^{(1)} \rangle + \frac{1}{2} \int \frac{\delta^2 E_{Hxc}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \rho^{(1)}(\mathbf{r})\rho^{(1)}(\mathbf{r}') d\mathbf{r}\,d\mathbf{r}', \tag{3}$$

$$E^{(4)} = \langle \phi^{(2)} | H_0 - E_0 | \phi^{(2)} \rangle + \langle \phi^{(2)} | H^1 | \phi^{(1)} \rangle + \langle \phi^{(1)} | H^1 | \phi^{(2)} \rangle + \frac{1}{2} \int \frac{\delta^2 E_{Hxc}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \rho^{(2)}(\mathbf{r})\rho^{(2)}(\mathbf{r}') d\mathbf{r}\,d\mathbf{r}'$$

$$+ \frac{1}{2} \int \frac{\delta^3 E_{Hxc}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')\delta\rho(\mathbf{r}'')} \rho^{(1)}(\mathbf{r})\rho^{(1)}(\mathbf{r}')\rho^{(2)}(\mathbf{r}'') d\mathbf{r}d\mathbf{r}'\,d\mathbf{r}''$$

$$+ \frac{1}{24} \int \frac{\delta^4 E_{Hxc}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')\delta\rho(\mathbf{r}'')\delta\rho(\mathbf{r}''')} \rho^{(1)}(\mathbf{r})\rho^{(1)}(\mathbf{r}')\rho^{(1)}(\mathbf{r}'')\rho^{(1)}(\mathbf{r}''') d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}''d\mathbf{r}''', \tag{4}$$

with

$$\rho^{(1)}(\mathbf{r}) = \phi_0^*(\mathbf{r})\phi^{(1)}(\mathbf{r}) + \phi^{(1)*}(\mathbf{r})\phi_0(\mathbf{r}) \tag{5}$$

and

$$\rho^{(2)}(\mathbf{r}) = \phi_0^*(\mathbf{r})\phi^{(2)}(\mathbf{r}) + \phi^{(2)*}(\mathbf{r})\phi_0(\mathbf{r}) + |\phi^{(1)}|^2. \tag{6}$$

It is easily seen that $E^{(2)}$ and $E^{(4)}$ vary quadratically [13] with respect to $\phi^{(1)}$ and $\phi^{(2)}$, respectively, near the minimum. Minimization is done with the constraint that the density change be such that the total number of electrons remain unchanged. Thus

$$\int \rho^{(1)}(\mathbf{r}) d\mathbf{r} = 0 \tag{7}$$

and

$$\int \rho^{(2)}(\mathbf{r}) d\mathbf{r} = 0. \tag{8}$$

Here

$$E_H = \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}\,d\mathbf{r}' \tag{9}$$

is the Hartree energy. For single-orbital, two-electron systems, the exchange energy within Hartree-Fock theory is

$$E_x^{HF}[\rho] = -\frac{1}{2} E_H[\rho]. \tag{10}$$

On the other hand,

$$E_x^{LDA}[\rho] = d_0 \int \rho^{4/3}(\mathbf{r}) d\mathbf{r}, \tag{11}$$

with $d_0 = -\frac{3}{4}(3/\pi)^{1/3}$. For correlation energy we use Gunnarson-Lundquist [13] parametrization so that

$$E_c^{LDA}[\rho] = c \int \rho(\mathbf{r}) \left[(1+x^3)\ln\left(1+\frac{1}{x}\right) + \frac{x}{2} - x^2 - \frac{1}{3} \right] d\mathbf{r}, \tag{12}$$

with $c = -0.0333$, $x = r_s/A$, $A = 11.4$, where $r_s = [3/4\pi\rho(\mathbf{r})]^{1/3}$ is the local r_s value. Functional derivatives of these functionals up to fourth order can be calculated in a straightforward manner.

Taking a cue from the hydrogen atom problem [20,21] we choose

$$\phi^{(1)}(\mathbf{r}) = \Delta_1(r)\phi_0(r)\cos\theta \tag{13}$$

TABLE I. Polarizability α and second hyperpolarizability γ for H$^-$, He, and Li$^+$ in Hartree-Fock theory. Results obtained from analytic Hartree-Fock wave functions are also given in the brackets. CHF refers to coupled Hartree-Fock theory. Numbers given are in atomic units.

Atom or ion	α			γ		
	Present work	CHF	Expt.	Present work	CHF	Expt.
H$^-$	91.40	91.39 [a]		6.33×10^6	4.37×10^6 [a]	
He	1.322	1.322 [b,c]	1.384 [d]	37.77	36.2 [b]	51.33 [e]
	(1.321)			(37.25)		
Li$^+$	0.1895	0.189 [c]	0.1911 [d]	0.2351		
	(0.1894)			(0.2354)		

[a]Reference 18.
[b]Reference 17.
[c]Reference 25.
[d]Reference 26.
[e]Reference 27.

and

$$\phi^{(2)}(\mathbf{r}) = [\Delta_2(r) + \Delta_3(r)\cos^2\theta]\phi_0(r) + \lambda\phi_0(r), \quad (14)$$

where

$$\Delta_1(r) = a_1 r + b_1 r^2 + c_1 r^3 + d_1 r^4 + e_1 r^5,$$

$$\Delta_2(r) = a_2 r + b_2 r^2 + c_2 r^3 + d_2 r^4 + e_2 r^5, \quad (15)$$

$$\Delta_3(r) = a_3 r + b_3 r^2 + c_3 r^3 + d_3 r^4 + e_3 r^5.$$

By minimizing $E^{(2)}$, parameters $a_1, \ldots, e_1$ are determined and kept fixed; $a_2, \ldots, e_2$ and $a_3, \ldots, e_3$ are then optimized to obtain $E^{(4)}$. Notice that with these choices of the induced wave functions Eq. (7) is automatically satisfied; to satisfy Eq. (8) λ is appropriately chosen for each set of parameters. α and γ are given by

$$\alpha = -2E^{(2)}, \quad \gamma = -24E^{(4)}. \quad (16)$$

We note here that such variational procedures have been employed [22] in the past to obtain dipole polarizabilities of atoms. However, what we show in this paper is that when extended further within DFT, they can also be applied to obtain higher-order polarizabilities. The approach in this paper also differs from other variational calculations [18,21] for γ within the Hartree-Fock theory: In those calculations a functional is constructed that gives the second-order perturbation equation upon optimization with respect to the orbitals. Thus the second-order orbitals are obtained from this functional rather than by directly minimizing the energy.

Results obtained by us are displayed in Tables I and II. Calculations have been performed on the 441 mesh of the Herman-Skillmann [23] atomic code. Convergence of the results has been tested by changing the number of parameters in Δ_1, Δ_2, and Δ_3. After five parameters, inclusion of more does not affect the value, as shown in Table III. Notice that Δ_1 also affects γ. Thus changing Δ_1 may not alter the value of α (change is quadratic) but changes γ.

In Table I we show the results of the present calculations within Hartree-Fock theory along with those of coupled Hartree-Fock (CHF) calculations [15–18]. It is evident that the values of α in the present work are the same as those obtained in CHF. On the other hand, the hyperpolarizability values are larger than those quoted in the literature for both H$^-$ and He. We suspect that the same would be the case for Li$^+$; the correlated wave-function calculation gives a value of 0.242 a.u., which should be larger than the HF result. As a check we have also calculated α and γ for He and Li$^+$ using analytic Hartree-Fock wave functions [24]. These results for γ, although slightly different (see Table I), are also larger than the values obtained in previous works. Further, they also show the sensitivity of hyperpolarizability on the zeroth-order wave function employed.

For H$^-$ α and γ are both quite large, consistent with H$^-$ being a diffused system as the extra electron is very loosely bound. Also the values are much smaller than the exact (correlated) theoretical value, which is a manifestation of the importance of Coulomb correlations in H$^-$.

The LDA results for the helium atom and lithium cation are displayed in Table II. There are no LDA numbers for H$^-$ because, as noted above, self-consistent LDA solutions

TABLE II. Polarizability α and second hyperpolarizability γ for He and Li$^+$ obtained within the LDA Kohn-Sham theory. TDLDA refers to results calculated by solving the Kohn-Sham equation to the appropriate order. Numbers given are in atomic units.

Atom or ion	α		γ	
	Present work	TDLDA	Present work	TDLDA
He	1.630	1.66 [a]	78.54	81.36 [b]
Li$^+$	0.2111		0.3535	

[a]Reference 10.
[b]Reference 12.

TABLE III. Convergence of polarizability α and second hyper-polarizability γ for He with respect to change in the number of parameters in Δ_1.

No. of parameters	α	γ
2	1.3218	42.95
3	1.3222	38.30
4	1.3222	37.67
5	1.3222	37.77
6	1.3222	37.76

for this ion cannot be obtained. Again, the numbers for He obtained by us are close to those calculated by solving the Kohn-Sham equation up to the appropriate order (to order 1 [10] for α and to order 3 [12] for γ). For Li$^+$, to the best of our knowledge, there are no published results. Further, it is clear that the LDA numbers are, particularly for γ, much larger than the CHF or the experimental [26,27] numbers. This is because the highest occupied orbital within the LDA is loosely bound. Further, since γ is more sensitive to the zeroth-order wave function, it differs relatively more than α.

In Table III the effect of change in Δ_1 on the value of α and γ for He is shown; in this calculation the number of parameters in Δ_2 and Δ_3 are kept unchanged. As noted above, α is not affected as appreciably with change in Δ_1 as

is γ. This is because, whereas changes in the value of α are quadratic in the difference between the variational and the exact $\phi^{(1)}$, it is not so for γ. The same trend is observed for the other systems.

We now address the question as to why our Hartree-Fock numbers are greater than 36.2 for He and 4.37×10^6 for H$^-$. These numbers are obtained by minimizing the total energy $\langle H + \lambda H^1 \rangle$ with respect to a variational wave function. On the other hand we are minimizing the correction of each order individually. Although in principle the numbers obtained by either method should be the same, it is possible that $E^{(4)}$(present work)$\leq E^{(4)}$(minimization of $\langle H + \lambda H^1 \rangle$) leading thereby to a better upper bound. Similarly in the variational calculations, as noted above, a constructed functional that is not the fourth-order energy is optimized to obtain second-order wave functions. This would clearly lead to fourth-order energies that are higher than those obtained by us by minimizing the energy directly.

To conclude we have demonstrated with the help of two-electron systems that the perturbation expansion of the variational principle can be used sequentially in a variational manner to obtain response functions of interacting electron systems. This makes computation of these quantities both more accurate and numerically much simpler. Encouraged by the present results, we are applying this method to other systems and will report the results in the future.

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