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Electric response properties of a confined gas of independent particles acted upon by a direct current electric field

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Abstract. Exact results for linear and nonlinear electric response properties of a non-interacting ensemble of charged particles, confined within an impenetrable box and subjected to a static, homogeneous electric field, are derived and discussed.

Key words: Static electric response – Polarizability and hyperpolarizability – Independent confined particles

1 Introduction

Very strong interest for a deeper understanding of the vast phenomenology associated with the interaction of intense electromagnetic (EM) fields with matter is widely documented in the literature. Besides obvious motivations of academic character, one realizes that behind such research effort stand prominent technological demands, many of them arising in modern materials science. In particular, the increasing role of nanostructured materials for the development of optical systems with desirable properties (large nonlinearities, fast response, etc.) gives rise to questions concerning the relation between their EM response properties and underlying electronic structure [1–8]. For this simple reason, the theoretical study of the behavior of charged carriers confined within small structures and subjected to external fields is recognized as being important and has determined the development of various models with the perspective of gaining insight into realistic situations.

We propose to deduce the exact electric response of a "gas" consisting of an arbitrary number of independent electrons, acted upon by a direct current electric field and confined within a one-dimensional box with infinitely high walls. The utility of this very schematic model is well known to both condensed-matter physicists and quantum chemists. For instance, delocalized π electrons in conjugated organic molecules have been roughly described in terms of noninteracting fermions moving within various networks (tube, toroidal "pillbox", more complex-shape geometries involving joints and branches), providing what is probably the simplest model of molecular electronic structure theory (free electron molecular orbital, FEMO model) [9, 10]. The recourse to this model for approximately describing the dielectric behavior of mesoscopic particles should also be pointed out [11–15]. The latter is actually the main reason for our interest, presently addressed at finding indications of the optical behavior of composite materials involving dispersions of metal nanoparticles.

The most conventional treatment leading to the various electric response coefficients is by quantum-mechanical perturbation theory, a procedure that in our case is rigorously feasible (even though troublesome for high-order coefficients). We follow here a different approach, based on the exact solution of the quantum-mechanical problem of a single electron acted upon by a static electric field. This problem, even though revisited many times (essentially for pedagogic motivations) [16–22], is briefly reconsidered in the next section so as to make this article self-contained. The extraction of both linear and nonlinear electric response coefficients (i.e. dipole polarizability and the first few hyperpolarizabilities) from the exact solution is carried out in Sect. 3, while some conclusive comments constitute the contents of the last section.

2 Quantum mechanics of a single confined particle subjected to an electric field

For a single particle (effective mass m and electric charge e) confined within a one-dimensional region between two impenetrable walls placed at $x = 0$, $x = L$ and subjected to a static, homogeneous electric field, E, the exact field-dressed orbitals $\phi_\varepsilon(x;F)$ satisfy the following Schrödinger equation

$$\frac{d^2\phi_\varepsilon(x;F)}{dx^2} + \frac{2m}{\hbar^2}[\varepsilon + Fx]\phi_\varepsilon(x;F) = 0 \ , \qquad (1)$$

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where $F = eE$ is the electric force acting on the particle and $\varepsilon = \varepsilon(F)$ is the energy eigenvalue.

By a simple change of variable, the general solution to Eq. (1) can be expressed in terms of the pair of independent solutions $Ai(z), Bi(z)$ to the Airy equation [23] as follows

$$\phi_\varepsilon(x;F) = NAi[-\beta(\varepsilon + Fx)] + MBi[-\beta(\varepsilon + Fx)] \ , \tag{2}$$

M and N being two constants and

$$\beta = \left(\frac{2m}{\hbar^2 F^2}\right)^{1/3} \ . \tag{3}$$

The boundary conditions $\phi_\varepsilon(0;F) = \phi_\varepsilon(L;F) = 0$ which apply to the problem lead to the secular equation

$$\begin{vmatrix} Ai(-\beta\varepsilon) & Bi(-\beta\varepsilon) \\ Ai[-\beta(\varepsilon + FL)] & Bi[-\beta(\varepsilon + FL)] \end{vmatrix} = 0 \ , \tag{4}$$

whose solution determines implicitly the allowed field-dressed energy eigenvalues, $\varepsilon_n(F)$.

For any eigenvalue ε_n, we have

$$\frac{M_n}{N_n} = -\frac{Ai(-\beta\varepsilon_n)}{Bi(-\beta\varepsilon_n)} = -\frac{Ai[-\beta(\varepsilon_n + FL)]}{Bi[-\beta(\varepsilon_n + FL)]} \ . \tag{5}$$

Equation (2) for the orbital $\phi_{\varepsilon_n}(x;F)$ is therefore usefully expressed as

$$\phi_{\varepsilon_n}(x;F) = N_n\left(Ai[-\beta(\varepsilon_n + Fx)] + \frac{M_n}{N_n}Bi[-\beta(\varepsilon_n + Fx)]\right) \ , \tag{6}$$

to be used in conjunction with Eq. (5). N_n is obviously fixed by normalizing the orbital $\phi_{\varepsilon_n}(x;F)$.

The expression for the centroid of any field-dressed orbital, $\langle x \rangle = \int_0^L \mathrm{d}x x|\phi_\varepsilon(x;F)|^2$, can be cast into the form

$$\langle x \rangle = \frac{N^2}{3\pi^2(\beta F)^2}\left(\frac{2\beta\varepsilon}{Bi^2(-\beta\varepsilon)} - \frac{\beta(2\varepsilon - FL)}{Bi^2[-\beta(\varepsilon + FL)]}\right) \ , \tag{7}$$

where, for the sake of simplicity, energy labels related to the specific state considered have been deleted. Equation (7) follows after a number of manipulations, where known exact results for indefinite integrals involving products of Airy functions $Ai(z)$ and/or $Bi(z)$ and powers have been used [24], along with the conditions expressed by Eq. (5) and the Wronskian property $W(Ai, Bi) = \pi^{-1}$.

A procedure entirely equivalent to that just described allows the squared normalization constant, N^2, to be expressed as

$$N^2 = \pi^2\beta F\left(\frac{1}{Bi^2(-\beta\varepsilon)} - \frac{1}{Bi^2[-\beta(\varepsilon + FL)]}\right)^{-1} \ . \tag{8}$$

At the cost of some additional labor, the orbital centroid can be given the following final form

$$\langle x \rangle(F) = \frac{2}{3}\frac{L}{2}\left(\frac{1}{1 - \left(\frac{Ai\{-\beta[\varepsilon(F)+FL]\}}{Ai[-\beta\varepsilon(F)]}\right)^2} - \frac{2\varepsilon(F)}{FL}\right) \ . \tag{9}$$

The presence in the denominator of the ratio involving squared Airy functions $Ai(z)$ with shifted arguments should be observed. In the latter equation, the F-dependence of the various quantities has been emphasized. The complicated F-dependence is hardly surprising considering that Eq. (9) is a rigorous result not affected by restrictions posed, for example, by perturbation-theory validity arguments.

3 Electric response properties according to the FEMO model

The FEMO model considered in this work is rather well known to condensed-matter physicists and quantum chemists [25, 26]. The acronym FEMO emphasizes a description characterized by the total neglect of inter-electronic repulsion effects and the consequent one-electron nature of the model. Accordingly, the electrons move independently, remaining confined within a box of appropriate size, and the ground-state electronic distribution follows simply by filling the lowest basic one-particle-in-a-box orbitals without violating the Pauli exclusion principle [26].

As the system becomes polarized due to the presence of an applied electric field, we assume the validity of the same building-up procedure just described, now in terms of field-dressed orbitals, i.e. polarized orbitals allowing the full effect of the applied field. If $2N$ denotes the number of electrons involved, the overall electric dipole moment can be expressed as follows (electronic charge $-e$),

$$\langle \mu \rangle = -2e\sum_{n=1}^{N}\langle x \rangle_n(F) \equiv 2\sum_{n=1}^{N}\langle \mu \rangle_n \ , \tag{10}$$

with the factor of 2 taking into account the spin degeneracy and $\langle x \rangle_n(F)$ being the centroid location of the nth field-dressed orbital, Eq. (9). Clearly, the evaluation of $\langle \mu \rangle$ would involve an exact diagonalization of the secular equation, Eq. (4). For not too high field strengths, however, $\langle \mu \rangle_n$ can be expanded conveniently in powers of the electric field $E = F/(-e)$,

$$\langle \mu \rangle_n \equiv \sum_{k=0}\frac{E^k}{k!}\mu_{kn} \ , \tag{11}$$

where $\mu_{kn} \equiv \left(\frac{\partial^k\langle \mu \rangle}{\partial E^k}\right)_{E=0}$. A truncation of the expansion after a few terms is expected a sufficiently accurate procedure in all practical applications.

To determine the desired electric response coefficients, we start from the following result for the energy of the nth orbital,

$$\varepsilon_n(F) = \varepsilon_n(0) - \sum_{k=0}\frac{E^{k+1}}{(k+1)!}\mu_{kn} \ , \tag{12}$$

a consequence of Hellmann–Feynman theorem [27] and Eq. (11). From Eq. (9), then we get in a straightforward way

$$\sum_{k=0}\frac{(3k+1)}{(k+1)!}\mu_{kn}E^k = -\left(\frac{eL}{v_n(F)} + \frac{2\varepsilon_n(0)}{E}\right) \ , \tag{13}$$

where we have set

$$v_n(F) = 1 - \left(\frac{Ai\{-\beta[\varepsilon_n(F) + FL]\}}{Ai[-\beta\varepsilon_n(F)]}\right)^2 \quad . \tag{14}$$

An expansion of the quantity on the right-hand side of Eq. (13) in powers of the electric field, E, leads finally to the following result for the coefficient of E^k in Eq. (10),

$$2\sum_{n=1}^{N} \mu_{kn} = -2\frac{(k+1)}{3k+1}\lim_{E\to 0}\sum_{n=1}^{N}\left[eL\left(\frac{\partial^k(1/v_n)}{\partial E^k}\right) + \frac{2(-1)^k\varepsilon_n(0)}{E^{k+1}}\right] \quad . \tag{15}$$

The electric polarizability, α, (linear response), the first hyperpolarizability, β, the second hyperpolarizability, γ, etc. (nonlinear response) correspond to $k=1, k=2$, $k=3$, etc., respectively, in Eq. (15).

Equation (15) is conveniently elaborated by considering the asymptotic behavior of $[Ai(-|x|)]^2, |x| \gg 1$. An ingenious treatment based on an integral representation of the squared Airy function [28, 29] yields

$$[Ai(-|x|)]^2 \cong \frac{|x|^{-1/2}}{2\pi}\left(1 + \sum_{p=1}^{\infty}\frac{(-1)^p(6p-1)!}{96^p p!|x|^{3p}}\right) \quad , \tag{16}$$

which allows $[v_n(F)]^{-1}$ to be expressed as a ratio of two asymptotic series involving the field E amplitude. At the cost of much paper and very annoying algebra, a procedure demanding much attention for capturing all the terms contributing to a given field power leads to the desired results

$$\alpha = \frac{L^4}{2\pi^2 a_0}\sum_{n=1}^{N}\left(-\frac{1}{3n^2} + \frac{5}{\pi^2 n^4}\right) \tag{17}$$

$$\beta = 0 \tag{18}$$

$$\gamma = \frac{L^{10}}{2\pi^6 e^2 a_0^3}\sum_{n=1}^{N}\left(-\frac{1}{3n^6} + \frac{70}{\pi^2 n^8} - \frac{660}{\pi^4 n^{10}}\right) \quad , \tag{19}$$

where $a_0 = \hbar^2/me^2$, the Bohr radius. We also find $\mu_{0n} = -eL/2$, as expected.

The exact response coefficients thus obtained involve contributions associated with the N lowest orbitals (doubly) occupied in the ground state. The result is in complete accordance with that obtained elsewhere in terms of a quantum-mechanical perturbation theory treatment [30]. The polarizability, α, of the model has actually been evaluated several times (sometimes incorrectly) [16, 18, 21, 22, 30, 31]. As far as the evaluation of the second hyperpolarizability is concerned, we are only aware of the result obtained in Ref. [30]. The fact that the first hyperpolarizability vanishes could be anticipated on the basis of simple symmetry arguments. For the model investigated, therefore, γ is the lowest nonlinear electric response coefficient different from zero, the same result holding for centrosymmetric systems [32].

Considering the following identities involving Riemann functions, $\varsigma(p)$, [23]

$$\sum_{n=1}^{\infty}\left(-\frac{1}{3n^2} + \frac{5}{\pi^2 n^4}\right) = -\frac{1}{3}\varsigma(2) + \frac{5}{\pi^2}\varsigma(4) = 0 \tag{20}$$

$$\sum_{n=1}^{\infty}\left(-\frac{1}{3n^6} + \frac{70}{\pi^2 n^8} - \frac{660}{\pi^4 n^{10}}\right) = -\frac{1}{3}\varsigma(6) + \frac{70}{\pi^2}\varsigma(8) - \frac{660}{\pi^4}\varsigma(10) = 0 \tag{21}$$

Equations (17)–(19) can also be expressed exactly in terms of contributions from unoccupied orbitals

$$\alpha = \frac{L^4}{2\pi^2 a_0}\sum_{n=N+1}^{\infty}\left(\frac{1}{3n^2} - \frac{5}{\pi^2 n^4}\right) \tag{22}$$

$$\gamma = \frac{L^{10}}{2\pi^6 e^2 a_0^3}\sum_{n=N+1}^{\infty}\left(\frac{1}{3n^6} - \frac{70}{\pi^2 n^8} + \frac{660}{\pi^4 n^{10}}\right) \tag{23}$$

Equations (22) and (23) constitute a more advantageous computational form in the case of systems containing a large number of electrons. Asymptotic expressions follow immediately from the previous equations by using the Euler–Maclaurin summation formula [23]. For large N, at the lowest order, we get

$$\alpha = \frac{L^4}{6\pi^2 a_0 N} = \frac{L^3}{6\pi a_0 k_F} \tag{24}$$

$$\gamma = \frac{L^{10}}{30\pi^6 e^2 a_0^3 N^5} = \frac{L^5}{30\pi e^2 a_0^3 k_F^5} \quad , \tag{25}$$

where $\hbar k_F \equiv \pi\hbar(N/L)$ is the Fermi momentum associated with the molecular electron distribution. It is also simply verified that the approximate expression for α thus obtained is very similar to that resulting from a highest occupied molecular orbital–lowest unoccupied molecular orbital perturbation theory calculation.

For fixed L, α and γ are seen to tend to zero as N tends to infinity, i.e. in the absence of unfilled orbitals. This result is hardly surprising because polarizability and hyperpolarizabilities correspond to distortion effects of the electron distribution, whose description intuitively requires the occurrence of virtual transitions from occupied to unoccupied orbitals. More interesting is the assumption that N/L is constant. The model now predicts a strong size-dependence of both linear and nonlinear electric response coefficients; in particular, one could conjecture $\gamma \propto \alpha^{5/3}$ [30, 33].

4 Some final comments

The quantum-mechanical study of a simple model constituted by a charged particle confined within a one-dimensional box and subjected to a static electric field offers an easy way for investigating the electric response of an independent electron system beyond the ordinary linear approximation, without recourse to perturbation-theory treatments requiring second-order corrections to the orbitals involved [30]. In particular, we have obtained expressions for the first two hyperpolarizabilities, which in realistic applications are all that is generally evaluated (at a very demanding cost).

For a harmonic-confinement model, i.e. a gas of noninteracting particles bound by harmonic forces to an attractive center, simple considerations establish that the electric response caused by a static electric field is only linear in the applied field, so any hyperpolarizability is now rigorously vanishing. Thus, the case considered in this work (impenetrable box) could be regarded as the simplest model capable of mimicking the behavior of realistic systems as far as the appearance of nonlinear electric effects is concerned.

According to Eqs. (17)–(19), the results for polarizability and hyperpolarizabilities follow in an additive form from contributions α_n and γ_n, which are not all necessarily positive. Actually, the only positive contribution, α_1, to α comes from the lowest filled orbital $(n = 1)$, while for the hyperpolarizability the situation is a bit more complicated. Now, in fact, γ_2, γ_3 and γ_4 are positive, while γ_1 and $\gamma_n (n \geq 5)$ are negative. Negative values for the polarizability mean that the probability of finding the electron on the left-hand side of the box $(x < L/2)$ is greater than on the right-hand side. The different (linear) response of a single quantum particle in the ground state and excited states has already been commented on [21, 22], particularly the similarity in behavior between a classical particle and a quantum particle in an excited state [22]. The permanence of the effect in the nonlinear-response regime, even though not surprising, is a result explicitly demonstrated in the present work.

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