Localized-orbital computation of linear and nonlinear susceptibilities

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Abstract

We present a method to compute high-order derivatives of the total energy which can be used in the framework of density functional theory. We provide a proof of the $2n + 1$ theorem for a general class of energy functionals in which the orbitals are not constrained to be orthonormal. Furthermore, by combining this result with a recently introduced Wannier-like representation of the electronic orbitals, we find expressions for the static linear and nonlinear susceptibilities which are much simpler than those obtained by standard perturbative expansions. We test numerically the validity of our approach with a 1D model Hamiltonian.

71.10+x, 71.20.Ad, 77.22-d
Perturbative techniques are usually applied to density functional theory (DFT)\textsuperscript{1,2} to study the response properties of materials from first principles. The evaluation of the second-order derivatives of the total energy yields phonon spectra,\textsuperscript{3} effective charges,\textsuperscript{3,4} dielectric constants,\textsuperscript{5,6} piezoelectric tensors\textsuperscript{7,8} and many other experimentally measurable quantities. Likewise the computation of higher-order derivatives permits the \textit{ab-initio} prediction of properties such as the Raman tensors,\textsuperscript{9} the second and higher-order susceptibilities, the nonlinear elastic constants etc..

There are already very sophisticated analytical methods to obtain the values of the second-order derivatives, and today it is possible to evaluate these quantities in systems with many atoms per unit cell.\textsuperscript{10} On the contrary, the evaluation of third or higher-order derivatives relies mainly on finite differences: the required derivatives are computed by numerical differentiation of the second-order derivatives. The cost of the finite differentiation limits the applicability of the technique to small systems and to short wavelength perturbations.

Closed-form expressions of the third or higher-order derivatives, obtained by a straightforward application of quantum-mechanical perturbation theory, are usually cumbersome. In the case of the second-order susceptibilities, i.e third order derivatives of the energy with respect to a uniform electric field, the perturbative expansion provides a formula which apparently diverges in the static limit. This divergence can be eliminated as shown in Ref. (11) in the context of a non self-consistent electronic structure theory. A specific application of the resulting formula has been performed using a semi-empirical tight-binding Hamiltonian.\textsuperscript{12} In order to extend this scheme to self-consistent DFT one has to face rather formidable formal difficulties. An explicit expression for the second-order susceptibility within DFT has been obtained using a software package for symbolic manipulation,\textsuperscript{13} and it has been applied by just one research group due to its complexity.\textsuperscript{14}

Alternative analytical expressions for the high-order derivatives of the energy are provided by the $2n + 1$ theorem, well known in standard perturbation theory for many years\textsuperscript{15} and recently rewritten in the language of DFT.\textsuperscript{16} This theorem states that the derivatives of
the energy up to order $2n + 1$ can be computed if the change of the wavefunctions is known up to order $n$. This approach appears particularly promising to compute high-order derivatives of the total energy with respect to an atomic displacement but, in the formulation of Ref. [16], it is of no practical use when the perturbation is an electric field. In fact the formulas contain the change of the eigenvalues of the Hamiltonian due to the perturbation, i.e. a quantity which is ill-defined when the perturbation is an electric field and the wavefunctions are Bloch states.

Recently new methods have been introduced in DFT to solve the electronic structure problem, mainly to reduce the number of operations necessary for the numerical solution. One of these methods [17] is based on a Wannier-like representation of the electronic orbitals which are constrained to be localized in finite regions of the real space. The localized states are in general nonorthonormal and are obtained from a direct minimization of the total energy of the system. The method is very convenient to study systems with many atoms since the localization of the wavefunctions allows the computation of the total energy with a workload proportional to the number of atoms. At the same time, the application of this technique to a periodic solid provides a good approximation for the Wannier functions which are usually difficult to obtain with other techniques. In Ref. [18] it was shown that the center of these Wannier-like functions yields the correct polarization of the system, and that their localization property can be conveniently used to study the behavior of a periodic insulating solid inside a uniform electric field. This approach allowed the computation of the physical properties of a solid under a finite electric field. The derivatives of the energy with respect to the electric field were computed by means of accurate finite difference calculations.

In this paper we further extend the approach of Ref. [18] and Ref. [16] and we give a method to compute analytically high-order derivatives of the energy. In particular we give a very general derivation of the $2n + 1$ theorem, which does not require the definition of a specific energy functional, contrary to what was done in previous work. We then apply our result to obtain the expressions for the linear and nonlinear susceptibilities in the Wannier-like representation of the electronic orbitals. The resulting expression for the second-order
susceptibility is much simpler than the one obtained by standard perturbation theory\[1\] because the use of the \(2n + 1\) theorem allows us to express this third-order derivative of the energy only as a function of the first order variation of the wavefunctions. Furthermore the use in the \(2n + 1\) theorem of Wannier-like functions instead of Bloch eigenfunctions\[16\] gives an expression for the second order susceptibility which is well defined also for the case when the perturbation is a uniform electric field.

We apply our results to a 1D model Hamiltonian to test the convergence properties of the proposed algorithm. We compute analytically the first-, second- and third-order derivatives of the total energy with respect to a uniform electric field and we compare the results with those of the finite difference calculations. The third-order derivative is computed for an arbitrary field, so that the fourth-order derivative is available as well through finite differences. The simplicity of our method makes it very well suited to compute high-order derivatives of the total energy for real materials in the framework of DFT.

We start with a general proof of the \(2n + 1\) theorem valid for an arbitrary total energy functional \(E(w, \lambda)\), where \(w\) is a vector whose elements are the coefficients of all the occupied wavefunctions on a given basis and \(\lambda\) is a parameter measuring the magnitude of the perturbation. We restrict ourselves to energy functionals where no explicit constraints—as for example those of orthonormalization—are imposed on the components of \(w\). For a given \(\lambda\) the total energy is defined as the minimum of \(E(w, \lambda)\) with respect to \(w\). If \(\lambda\) is varied from \(\lambda^{(0)}\) to \(\lambda^{(0)} + \Delta \lambda\), the vector \(w\) which minimizes the energy functional will change from \(w^{(0)}\) to \(w^{(0)} + \Delta w\). We can expand the total energy around \(w^{(0)}\) by a Taylor series:

\[
E(w^{(0)} + \Delta w, \lambda^{(0)} + \Delta \lambda) = \sum_{p=0}^{\infty} \sum_{k=0}^{\infty} \frac{1}{k! p!} \delta^{k+p} E(w^{(0)}, \lambda^{(0)}) (\Delta w)^k (\Delta \lambda)^p,
\]

(1)

where we use the notation: \(\delta^{k} E(\Delta w)^k = (\sum_i \Delta w_i \frac{\partial}{\partial w_i})^k E\). At a given \(\Delta \lambda\) the force is defined by:

\[
f = \frac{\partial E(w^{(0)} + \Delta w, \lambda^{(0)} + \Delta \lambda)}{\partial (w^{(0)} + \Delta w)} = \sum_{p=0}^{\infty} \sum_{k=1}^{\infty} \frac{1}{(k-1)! p!} \delta^{k+p} E(w^{(0)}, \lambda^{(0)}) (\Delta w)^{k-1} (\Delta \lambda)^p.
\]

(2)

The vector \(\Delta w\) is the solution of the equation obtained from the extremum condition \(f = 0\).
We now define $f^{(n)}$ and $E^{(n)}$ as the force and the energy to order $n$ in $\Delta \lambda$. Explicit expressions of these quantities are obtained by writing $\Delta w$ as:

$$\Delta w = w^{(1)} + w^{(2)} + \ldots,$$

where $w^{(n)}$ is of order $(\Delta \lambda)^n$, and by separating the various orders in Eq. (1) and Eq. (2). $w^{(n)}$ is obtained from the equation $f^{(n)} = 0$. Using these definitions the proof of the $2n + 1$ theorem is straightforward.

Since the term quadratic in $w^{(l)}$ is of order $(\Delta \lambda)^{2l}$, $E^{(2n+1)}$ can contain $w^{(l)}$ only at linear order if $l > n$. Under the same condition, we show that the coefficient of $w^{(l)}$ in $E^{(2n+1)}$ is zero. To show this it is useful to single out $w^{(l)}$ from the product $(\Delta w)^k$ appearing in Eq. (1), using the relation:

$$(\Delta w)^k = (\Delta w - w^{(l)} + w^{(l)})^k = kw^{(l)}(\Delta w)^{k-1} + (\Delta w - w^{(l)})^k + o((\Delta \lambda)^{2n+1}),$$

which is valid for $l > n$. The only term which is linear in $w^{(l)}$ is the first term of the r.h.s. of Eq. (4). Inserting this term in Eq. (1) and recalling the definition of $f$, Eq. (2), we can write $E^{(2n+1)}$ as:

$$E^{(2n+1)} = w^{(2n+1)}f^{(0)} + \ldots + w^{(l)}f^{(2n+1-l)} + \ldots + w^{(n+1)}f^{(n)} + P^{(2n+1)}(w^{(1)}, \ldots , w^{(n)}),$$

where $P^{(2n+1)}$ is a polynomial of degree $2n + 1$. Since $f^{(i)} = 0$ for every $i$, due to the extremum condition, we obtain

$$E^{(2n+1)} = P^{(2n+1)}(w^{(1)}, \ldots , w^{(n)}).$$

This completes the proof of the $2n + 1$ theorem. We note that our formulation does not require any hypothesis on the specific form of the energy functional. Therefore our proof can be applied to DFT, to correlated wavefunctions, and also in contexts other than quantum theory. Furthermore the present approach combined with a functional with implicit orthonormalization constraints can be used to derive the perturbative expansion in cases where the standard approach is cumbersome, e.g. the case of DFT when the atoms are described by Vanderbilt pseudopotentials.
We now apply the above ideas to the computation of the linear and nonlinear susceptibilities. As explained in Ref. \[18\] it is possible to define a total energy functional for a periodic insulating solid in a finite electric field as:

\[
E(|w_0\rangle, F) = \sum_l \langle w_0|H + eFx|w_l\rangle(2\delta_{0,l} - \langle w_l|w_0\rangle),
\]

where \(H\) is the unperturbed Hamiltonian of the solid, \(F\) is the electric field, \(x\) is the position operator, \(e\) is the electron charge and \(|w_l\rangle\) are Wannier-like functions associated to the direct lattice vector \(R_l\), which are in general non-orthonormal. The Wannier function \(|w_l\rangle\) is obtained by translating the function centered at the origin by a vector \(R_l\). \(|w_0\rangle\) is free to vary within a real space localization region (LR) of radius \(R_c\) centered at the origin and it is set equal to zero outside LR. For simplicity in Eq. (7) we assume that only the lowest band is filled, that the system is one-dimensional and that the total energy describes independent electrons. Self consistency does not yield any additional problem. We stress here that the expectation value of \(x\) is well defined for any finite cut-off radius \(R_c\). Furthermore we note that even if no orthogonality constraints are imposed on the \(|w_l\rangle\), at the minimum they become approximately orthonormal as shown in Ref. \[17\]}

We now recall that the linear and the quadratic susceptibilities \(\chi^{(1)}\) and \(\chi^{(2)}\), are obtained as \(\frac{1}{2}\chi^{(1)}(\Delta F)^2 = E^{(2)}\) and \(\frac{1}{3}\chi^{(2)}(\Delta F)^3 = E^{(3)}\) where \(E^{(n)}\) is the variation of the energy functional given in Eq. (7) to order \(n\) in the perturbing field \(\Delta F\). From Eq. (7) and Eq. (8) with \(\Delta \lambda = \Delta F\), we obtain the expressions:

\[
\frac{1}{2}\chi^{(1)}(\Delta F)^2 = \frac{1}{2} \frac{\delta^2 E}{\delta w^2}(w^{(1)})^2 + \frac{\delta^2 E}{\delta w \delta F}w^{(1)}\Delta F,
\]

\[
\frac{1}{3}\chi^{(2)}(\Delta F)^3 = \frac{1}{6} \frac{\delta^3 E}{\delta w^3}(w^{(1)})^3 + \frac{1}{2} \frac{\delta^3 E}{\delta w^2 \delta F}(w^{(1)})^2 \Delta F,
\]

where we used the fact that the total energy functional is linear in the electric field. The first order variation of the localized orbitals \(w^{(1)}\) is obtained either from the condition \(f^{(1)} = 0\) as the solution of a linear system:

\[
\frac{\delta^2 E}{\delta w^2}w^{(1)} + \frac{\delta^2 E}{\delta w \delta F}\Delta F = 0,
\]
or from a direct minimization of $E^{(2)}$, Eq. (8), with respect to $w^{(1)}$ as in Ref. [10]. All the energy derivatives appearing in these formulas are evaluated at the unperturbed vector $w^{(0)}$.

We applied the above results to a 1D model with Hamiltonian $H = -\nabla^2 + V(x)$ where $V(x)$ is a periodic potential with period 3, i.e., $V(x + 3) = V(x)$. We chose $V(x) = -\Delta$ if $x \in (-1.5, -0.5]$, $V(x) = \alpha - \Delta$ if $x \in (-0.5, 0.5]$, and $V(x) = 0$ if $x \in (0.5, 1.5]$. The parameter $\Delta$ is kept fixed at the value $\Delta = 4$ and $\alpha$ varies between $\alpha = 0$ and $\alpha = \Delta$.

At the two limiting values, the model has inversion symmetry, and therefore $\chi^{(2)} = 0$. Otherwise the parameter $\alpha$ tunes the value of $\chi^{(2)}$. We discretized the wavefunctions $w(x)$ on a $N$-point mesh $x_i$ with equal spacing $\Delta x$. In this representation the action of the Laplacian operator on the wavefunctions is modelled as a finite difference: $\nabla^2 w(x_i) = (w(x_{i+1}) + w(x_{i-1}) - 2w(x_i))/((\Delta x)^2)$. All the calculations are made with $\Delta x = 1/3$.

In Fig. 1 we show the $\chi^{(1)}$ values computed from the analytical derivative of the total energy, Eq. (8). These are compared with the $\chi^{(1)}$ values obtained from a numerical differentiation of the polarization $P = \delta E/\delta F$ computed at finite electric fields. The two results are in perfect agreement. We note that the finite difference calculation yields the same $\chi^{(1)}$ as a perturbative approach based on Bloch wavefunctions.[8]

In the same figure we also show a comparison between the values of $\chi^{(2)}$, as obtained from the analytical derivative, Eq. (9), and from a numerical differentiation of the values of $\chi^{(1)}$ computed at finite electric fields. Even in this case the two calculations are in perfect agreement.

In Fig. 2 we present the values of $\chi^{(2)}$ as a function of the electric field for $\alpha = 2$: its linearity around the origin allows us to extract from the slope of the curve the value of $\chi^{(3)} = \frac{2}{3} \frac{d\chi^{(2)}}{dF}$.

All the above calculations have been done with an $R_c$ value such that the LR includes seven unit cells. As shown in Ref. [18] the main concern in this type of calculations is the convergence rate of the studied quantities with respect to the dimensions of the LR. In Fig. 3 we show how the values of $\chi^{(2)}$ converge as a function of the size of the LR.
In conclusion we gave a new proof of the $2n + 1$ theorem. We applied it to the total energy of an insulator in a uniform electric field where the wavefunctions are described by localized orbitals, with no explicit orthonormalization constraints. We provided a method to compute analytically the first and second-order susceptibilities, which is much simpler than the standard approach. We tested its accuracy and convergence properties in a 1D model Hamiltonian. We believe that the application of this method to DFT and to an arbitrary kind of perturbation could open the way to a simple and reproducible computation of high-order derivatives of the total energy. This will be an efficient way to compute important properties of real materials such as the Raman tensors or the nonlinear susceptibilities even in systems with complex unit cells.

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FIGURES

FIG. 1. Linear (dashed line) and quadratic (solid line) susceptibilities of the model system computed analytically with Eqs. (8), (9). The results obtained from numerical differentiation of the polarization (solid squares) and of the linear susceptibility (open squares), both computed in finite electric fields, are also shown.

FIG. 2. Quadratic susceptibility as a function of the electric field for $\alpha = 2$.

FIG. 3. Quadratic susceptibility as a function of the parameter $\alpha$ for several dimensions of the localization regions. The curves refers to a localization region equal to three (long dashed), five (dotted), seven (dashed) and nine (solid line) unit cells, respectively.