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Wannier and Bloch orbital computation of the nonlinear susceptibility

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We present a method to compute high-order derivatives of the total energy of a periodic solid with respect to a uniform electric field. We apply the $2n+1$ theorem to a recently introduced total energy functional which uses a Wannier representation for the electronic orbitals and we find an expression for the static nonlinear susceptibility which is much simpler than the one obtained by standard perturbative expansions. We show that the zero-field expression of the nonlinear susceptibility can be rewritten in a Bloch representation. We test numerically the validity of our approach with a 1D model Hamiltonian.

Perturbative techniques are usually applied to density functional theory[1,2] (DFT) to study the response properties of materials from first principles. The evaluation of the second-order derivatives of the total energy yields phonon spectra,[3] effective charges,[3,4] dielectric constants,[5,6] piezoelectric tensors,[7,8] and many other experimentally measurable quantities. Likewise the computation of higher-order derivatives permits the *ab initio* prediction of properties such as the Raman tensors,[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.[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 semiempirical tight-binding Hamiltonian.[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,[13] and it has been applied by just one research group due to its complexity.[14]

Alternative analytical expressions for the high-order derivatives of the energy are provided by the $2n+1$ theorem, well known in quantum chemistry[15] and recently rewritten in the language of DFT.[16] This theorem states that the derivatives of the energy up to order $2n+1$ can be computed if the change of the wave functions 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 wave functions are Bloch states.

Recently 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 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 wave functions allows the computation of the total energy with a work load 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 functions yields the correct polarization of the system,[20] 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.[18]

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 with respect to the electric field. Using the $2n+1$ theorem we obtain well-defined expressions of the linear and nonlinear susceptibilities in the Wannier representation of the electronic orbitals.[17,18] Furthermore we rewrite the zero-field expression of the nonlinear susceptibility in a Bloch representation. To this purpose we apply a procedure which was used in Refs. 19 and 20 to relate the center of the Wannier functions to a Berry phase. Our formulas for the second-order susceptibility are much simpler than those obtained by standard perturbation theory 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 wave functions.

We apply our results to a one-dimensional (1D) model Hamiltonian to test the convergence properties of the proposed algorithm. We compute analytically, in the Wannier representation, 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. Furthermore, we test numerically the equivalence between the expression of the nonlinear susceptibility as obtained in a Wannier and in a Bloch representation.

Following Ref. 15 we state the $2n+1$ theorem in the form applicable to an unconstrained total energy functional $E[\mathbf{w},\lambda]$, where $\mathbf{w}$ is a vector whose elements are the coefficients of all the occupied wave functions on a given basis and λ is a parameter measuring the magnitude of the perturbation. For a given λ the total energy is defined as the minimum of $E[\mathbf{w},\lambda]$ with respect to $\mathbf{w}$. If λ is varied from $\lambda^{(0)}$ to $\lambda^{(0)}+\Delta\lambda$, the vector $\mathbf{w}$ which minimizes the energy functional will change from $\mathbf{w}^{(0)}$ to $\mathbf{w}^{(0)}+\Delta\mathbf{w}$. We can expand the total energy around $\mathbf{w}^{(0)}$ by a Taylor series:

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

where we use the notation $(\delta^{k}E/\delta\mathbf{w}^{k})(\Delta\mathbf{w})^{k}=(\Sigma_i\Delta w_i\partial/\partial w_i)^{k}E$. We now define $E^{(n)}$ as the variation of the energy of order n in $\Delta\lambda$. An explicit expression of this quantity is obtained by writing $\Delta\mathbf{w}$ as

$$\Delta\mathbf{w}=\mathbf{w}^{(1)}+\mathbf{w}^{(2)}+\cdots, \quad (2)$$

where $\mathbf{w}^{(n)}$ is of order $(\Delta\lambda)^{n}$. Since $\Delta\mathbf{w}$ minimizes the total energy, we have

$$E[\mathbf{w}^{(0)}+\Delta\mathbf{w},\lambda^{(0)}+\Delta\lambda]=E[\mathbf{w}^{(0)}+\Delta\mathbf{w}+O(\Delta\lambda^{n+1}),\lambda^{(0)}+\Delta\lambda]+O(\Delta\lambda^{2n+2}). \quad (3)$$

Therefore, the energy is exact up to order $2n+1$ if we substitute Eq. (2) only up to order n in Eq. (1). In this way we write $E^{(2n+1)}$ as a polynomial of degree $2n+1$ in the arguments $\mathbf{w}^{(1)},\ldots,\mathbf{w}^{(n)}$.

Applying this formulation of the $2n+1$ theorem to the self-consistent energy functional with no explicit orthonormalization constraints presented in Ref. 17, we can obtain an explicit expression for $E^{(n)}$ within DFT just by computing simple partial derivatives. This is useful 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.[21]

We now apply the above theorem 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

$$E[\mathbf{w},F]=\sum_{m,n=1}^{M}\sum_{l}\langle w_{0,m}|H+eFx|w_{l,n}\rangle\times(2\delta_{l,0}\delta_{n,m}-\langle w_{l,n}|w_{0,m}\rangle), \quad (4)$$

where H is the unperturbed Hamiltonian of the solid, F is the electric field, x is the position operator, e is the electron charge, M is the number of occupied bands, and $|w_{l,n}\rangle$ is the Wannier function of the band n associated with the direct lattice vector R_l. The $|w_{l,n}\rangle$ are in general nonorthonormal. The Wannier function $|w_{l,n}\rangle$ is obtained by translating the function centered at the origin by a vector R_l. $|w_{0,n}\rangle$ 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. (4) we assume 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 cutoff radius R_c. Furthermore we note that even if no orthogonality constraints are imposed on the $|w_{l,n}\rangle$, at the minimum they become approximately orthonormal.[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. (4) to order n in the perturbing field ΔF. From Eq. (1) with $\Delta\lambda=\Delta F$, we obtain the expressions

$$-\frac{1}{2}\chi^{(1)}(\Delta F)^2=\frac{1}{2}\frac{\delta^2E}{\delta\mathbf{w}^2}(\mathbf{w}^{(1)})^2+\frac{\delta^2E}{\delta\mathbf{w}\delta F}\mathbf{w}^{(1)}\Delta F, \quad (5)$$

$$-\frac{1}{3}\chi^{(2)}(\Delta F)^3=\frac{1}{6}\frac{\delta^3E}{\delta\mathbf{w}^3}(\mathbf{w}^{(1)})^3+\frac{1}{2}\frac{\delta^3E}{\delta\mathbf{w}^2\delta F}(\mathbf{w}^{(1)})^2\Delta F, \quad (6)$$

where we used the fact that the total energy functional is linear in the electric field. As shown in Ref. 10, the first-order variation of the localized orbitals $\mathbf{w}^{(1)}$ is obtained by minimizing $E^{(2)}$ with respect to $\mathbf{w}^{(1)}$. This condition is equivalent to the equation $\delta E^{(2)}/\delta\mathbf{w}^{(1)}=0$.

At zero electric field Eq. (6) can be transformed in an expression which contains only the unperturbed Bloch orbitals and their first-order variations projected on the conduction band. If we perform first the limit where the electric field goes to zero and then the limit where R_c goes to infinity, the Wannier functions $|w_{l,n}\rangle$ become orthonormal.[17] Therefore we can write the relationships

$$\langle w_{l,n}^{(0)}|w_{0,m}^{(0)}\rangle=\delta_{l,0}\delta_{n,m},$$
$$\langle w_{l,n}^{(0)}|w_{0,m}^{(1)}\rangle+\langle w_{l,n}^{(1)}|w_{0,m}^{(0)}\rangle=0. \quad (7)$$

These equations are useful to simplify the condition $\delta E^{(2)}/\delta\mathbf{w}^{(1)}=0$ which now reads

$$-QeAFx|w_{0,m}^{(0)}\rangle = HQ|w_{0,m}^{(1)}\rangle - \sum_{n=1}^{M}\sum_{l} Q|w_{l,n}^{(1)}\rangle\langle w_{l,n}^{(0)}|H|w_{0,m}^{(0)}\rangle, \quad (8)$$

where $Q=1-\Sigma_{n=1}^{M}\Sigma_l|w_{l,n}^{(0)}\rangle\langle w_{l,n}^{(0)}|$ is the projector on the conduction bands. Using Eq. (7) and Eq. (8), we can write Eq. (6) in a form which contains only the projection of $|w_{l,m}^{(1)}\rangle$ on the unperturbed conduction bands:[22]

$$-\frac{1}{3}\chi^{(2)}(\Delta F)^2 = \sum_{m=1}^{M} e\langle w_{0,m}^{(1)}|QxQ|w_{0,m}^{(1)}\rangle - \sum_{m,n=1}^{M}\sum_{l} e\langle w_{0,m}^{(0)}|x|w_{l,n}^{(0)}\rangle \times \langle w_{l,n}^{(1)}|Q|w_{0,m}^{(1)}\rangle. \quad (9)$$

We now express this formula with Bloch orbitals. We recall that the Wannier functions are defined in terms of the Bloch functions $\psi_{k,n}(x)$ as

$$w_{0,n}(x)=\frac{\Omega}{2\pi}\int_{\mathrm{BZ}} dk\,\psi_{k,n}(x), \quad (10)$$

where the integral is done over the first Brillouin zone (BZ), Ω is the dimension of the unit cell, the Bloch functions are normalized on the unit cell, and $\psi_{k+G,n}(x)=\psi_{k,n}(x)$; here G is a reciprocal lattice vector. Inserting this definition in Eq. (9) and using the relationship $x\psi_{k,n}(x) = -(i\partial/\partial k)\psi_{k,n}(x)+e^{ikx}(i\partial/\partial k)u_{k,n}(x)$, where $u_{k,n}(x) = e^{-ikx}\psi_{k,n}(x)$ are the periodic parts of the Bloch wave functions, we eventually obtain

$$-\frac{1}{3}\chi^{(2)}(\Delta F)^2 = -i\frac{e\Omega}{2\pi}\sum_{m,n=1}^{M}\int_{\mathrm{BZ}} dk \times\left\langle u_{k,m}^{(0)}\left|\frac{\partial}{\partial k}(|u_{k,n}^{(0)}\rangle\langle\tilde{u}_{k,n}^{(1)}|)\right|\tilde{u}_{k,m}^{(1)}\right\rangle, \quad (11)$$

where $|\tilde{u}_{k,m}^{(1)}\rangle=|u_{k,m}^{(1)}\rangle-\Sigma_{n=1}^{M}|u_{k,n}^{(0)}\rangle\langle u_{k,n}^{(0)}|u_{k,m}^{(1)}\rangle$ is the perturbed orbital projected on the unperturbed conduction bands.

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 Δ is kept fixed at the value $\Delta=4$ and α 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 α tunes the value of $\chi^{(2)}$. We discretized the wave functions $w(x)$ on a mesh x_i with equal spacing Δx. In this representation the action of the Laplacian operator on the wave functions is modeled 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 one occupied band, $\Delta x=1/3$ and $e=1$.

In Fig. 1 we show the $\chi^{(1)}$ values computed from the analytical derivative of the total energy in the Wannier representation, Eq. (5). 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.

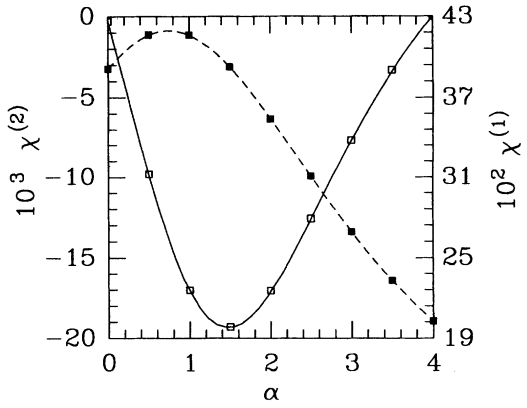

FIG. 1. Linear (dashed line) and quadratic (solid line) susceptibilities of the model system computed analytically in the Wannier representation, Eqs. (5) and (6). The results obtained from numerical differentiation of the polarization (solid squares) and of the linear susceptibility (open squares), both computed in finite electric fields, are also shown.

In the same figure we also show a comparison between the values of $\chi^{(2)}$, as obtained from the analytical derivative, Eq. (6), and from a numerical differentiation of the values of $\chi^{(1)}$ computed at finite electric fields. Also in this case the two calculations are in perfect agreement.

Using Eq. (6) it is possible to evaluate the values of $\chi^{(2)}$ for a given finite electric field. Therefore we can compute the value of $\chi^{(3)}=\frac{2}{3}d\chi^{(2)}/dF$ by finite differences. At $\alpha=2$ we obtained $\chi^{(3)}=1.0$.

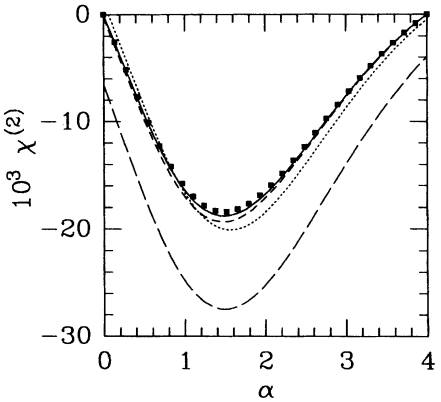

FIG. 2. Quadratic susceptibility computed in the Wannier representation, Eq. (6), as a function of the parameter α for several dimensions of the localization regions. The curves refer to a localization region equal to three (long dashed), five (dotted), seven (dashed), and nine (solid line) unit cells, respectively. The filled squares are the results obtained in the Bloch representation, Eq. (12), with 20 k points.

All the above calculations have been done with an R_c value such that the LR includes seven unit cells. In Fig. 2 we show how the values of $\chi^{(2)}$ converge as a function of the size of the LR.

In Fig. 2 we plot also the values of the $\chi^{(2)}$ computed in the Bloch representation. We discretized the integral and the derivative appearing in Eq. (11) on a uniform k-point mesh k_i, obtaining

$$-\frac{1}{3}\chi^{(2)}(\Delta F)^2=\frac{e\Omega}{2\pi}\mathrm{Im}\sum_{m,n=1}^{M}\sum_{i}\langle u^{(0)}_{k_i,m}|u^{(0)}_{k_{i+1},n}\rangle \times\langle\tilde{u}^{(1)}_{k_{i+1},n}|\tilde{u}^{(1)}_{k_i,m}\rangle. \quad (12)$$

Here the $|u^{(0)}_{k,n}\rangle$ were computed diagonalizing the unperturbed Hamiltonian and the $|\tilde{u}^{(1)}_{k,n}\rangle$ were computed by standard perturbation theory. The $\chi^{(2)}$ computed with 20 k points coincides, within the convergence error, with the result obtained with Wannier orbitals.

In conclusion we applied the $2n+1$ theorem to a periodic insulator in a uniform electric field where the wave functions are described by localized Wannier orbitals. In this Wannier representation we provided a method to compute analytically the first- and second-order susceptibilities for a given electric field. Furthermore, in the special case where this field is taken as zero, we rewrote the expression of the nonlinear susceptibility in a Bloch representation. With respect to previous approaches for the calculation of nonlinear susceptibilities, our method avoids completely perturbation sums, and has a simple expression in terms of the *linear* variation of the occupied orbitals, a quantity which is nowadays accessible in various computational frameworks. The accuracy of our method has been tested in a 1D model Hamiltonian. We believe that the application of our method to state-of-the-art DFT could open the way to a simple and reproducible computation of high-order derivatives of the total energy such as the Raman tensors or the nonlinear susceptibilities even in systems with complex unit cells.

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