

## ***Ab initio* Molecular Dynamics in a Finite Homogeneous Electric Field**

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We treat homogeneous electric fields within density functional calculations with periodic boundary conditions. A nonlocal energy functional depending on the applied field is used within an *ab initio* molecular dynamics scheme. The reliability of the method is demonstrated in the case of bulk MgO for the Born effective charges, and the high- and low-frequency dielectric constants. We evaluate the static dielectric constant by performing a damped molecular dynamics in an electric field and avoiding the calculation of the dynamical matrix. Application of this method to vitreous silica shows good agreement with experiment and illustrates its potential for systems of large size.

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Density functional calculations applied to periodic solids have demonstrated their reliability in describing material properties and have become a routinely used tool for investigation. However, the application of these methods to systems in an external electric field have remained limited, in sharp contrast with the widespread use of electric fields in experimental setups. Several theoretical studies have shown that it is possible to account for the effect of an electric field within a perturbational approach [1–5]. However, the study of dynamical transformations in an electric field would greatly benefit from the possibility of considering *finite* fields. In fact, the energy of the electronic ground state in an extended electric field does not have a lower bound [6–8]. Nonetheless, it is of interest to describe the long-living metastable physical state which arises in response to the field [7,8]. The difficulty of treating finite electric fields is related to the intrinsic nonperiodic nature of the position operator. The advent of the modern theory of polarization [9,10] has revitalized the study of electric fields in periodic electronic structure calculations [8,11–13]. In particular, Nunes and Gonze [12] introduced a periodic energy functional depending on the applied electric field and recovered the same derivatives with respect to the field as given by more conventional perturbational methods [2,4].

We introduce here an energy functional to treat *finite* electric fields in first-principles electronic structure calculations. We prove that its derivatives with respect to the field coincide with those of perturbational approaches [2,4,5,12] for any order of perturbation. The present functional provides a practical way for investigating dielectric properties. Furthermore, by calculating derivatives with respect to atomic positions, we show that this functional is suitable for application in *ab initio* molecular dynamics schemes [14]. Using bulk MgO as a test case, we calculate by finite differences the high-frequency dielectric constant and the Born effective charges, and find excellent accord with results obtained with perturbational methods. We also show how the static dielectric constant can be

obtained by performing a molecular dynamics relaxation, entirely avoiding the calculation of normal modes. To illustrate the potential of our scheme for systems of large size, we calculate the high- and low-frequency dielectric constants for a model of vitreous silica, finding good agreement with experiment.

For a system obeying periodic boundary conditions, we describe its metastable state induced by the presence of a finite electric field  $\mathcal{E}$  (taken along  $x$ ) by the variational energy functional,

$$E^{\mathcal{E}}[\{\psi_i\}] = E^{(0)}[\{\psi_i\}] - \mathcal{E} \cdot P[\{\psi_i\}], \quad (1)$$

where  $E^{(0)}[\{\psi_i\}]$  is the usual energy functional in the absence of an electric field and  $P[\{\psi_i\}]$  the polarization along the direction of  $\mathcal{E}$ , as defined by Resta [15]:

$$P[\{\psi_i\}] = -\frac{L}{\pi} \text{Im}(\ln \det S[\{\psi_i\}]), \quad (2)$$

where  $L$  is the periodicity of the cell and  $S[\{\psi_i\}]$  a matrix calculated for the set of doubly occupied wave functions  $\{\psi_i\}$ :

$$S_{ij} = \langle \psi_i | e^{2\pi i x/L} | \psi_j \rangle. \quad (3)$$

For simplicity, we consider here cubic unit cells. The same functional as in (1) was studied in Ref. [5] within a perturbational approach. In parallel with our work, a functional similar to (1) was used in Ref. [13], with wave functions restricted to Bloch symmetry [12].

It is of interest to compare our formulation with the periodic perturbation used by Nunes and Gonze [12], as well as with the more conventional perturbational methods [2,4]. We first consider the case of a vanishing electric field. Applied to a crystalline system with periodicity  $a$  in the direction of the field, with  $L = Na$ , the definition (2) of the polarization coincides with that of Nunes and Gonze provided a discrete number  $N$  of equally spaced  $k$  points are used [15]. However, when the field is turned on, the states  $\{\psi_i\}$  minimizing the functional (1) do not

necessarily carry the Bloch symmetry. This enhanced variational freedom constitutes, in principle, a *qualitative* difference with respect to approaches in which the perturbation is assumed to preserve the periodicity  $a$  of the minimal unit cell from the outset [2,4,12,13].

We now show that, in the limit  $N \rightarrow \infty$ , the derivatives of the energy (1),

$$E^{(n)} = \frac{1}{n!} \lim_{N \rightarrow \infty} \left. \frac{d^n E_N^\mathcal{E}}{d\mathcal{E}^n} \right|_{\mathcal{E}=0}, \quad (4)$$

at vanishing field, coincide with those resulting from the periodic perturbation of Nunes and Gonze [12], and consequently with those given by conventional perturbational methods [2,4]. This indicates that the result obtained with a periodic scheme is recovered identically *even when the periodic symmetry is relaxed*.

For the lowest orders,  $E^{(0)}$  and  $E^{(1)}$  depend only on the unperturbed eigenstates  $\{\psi_i^{(0)}\}$ , which obey the Bloch symmetry. The equivalence with perturbational methods can then be demonstrated as in Ref. [15]. We extend the correspondence to the second and third orders of the energy by considering an expansion of the perturbed wave functions  $\psi_i^\mathcal{E}$  up to first order in  $\mathcal{E}$  [16]. For a crystalline system with  $L = Na$ ,

$$|\psi_i^\mathcal{E}\rangle = e^{ik_i x} |u_i^{(0)}\rangle + \mathcal{E} \sum_{k'} e^{ik' x} |u_{k_i \rightarrow k'}^{(1)}\rangle + O(\mathcal{E}^2), \quad (5)$$

where the functions  $u_i^{(0)}$  and  $u_{k_i \rightarrow k'}^{(1)}$  are periodic with periodicity  $a$ , and the sum runs over  $k' = 2\pi n/L$  with  $n = 0, \dots, N-1$ . The expansion in (5) explicitly allows for mixing between different  $k$  points. At second order, the perturbation term in (1) gives

$$2 \frac{dP}{d\mathcal{E}} \Big|_{\mathcal{E}=0} = -\frac{2L}{\pi} \text{Im} \frac{1}{D^{(0)}} \frac{d}{d\mathcal{E}} \det S[\{\psi_i^\mathcal{E}\}] \Big|_{\mathcal{E}=0}, \quad (6)$$

where  $D^{(0)} = \det S[\{\psi_i^{(0)}\}]$ . When replacing (5) in (6), only terms diagonal in  $k$  survive, i.e.,

$$|u_{k_i \rightarrow k'}^{(1)}\rangle = \delta_{k_i, k'} |u_{k_i \rightarrow k_i}^{(1)}\rangle, \quad (7)$$

owing to the property that the operator  $e^{2\pi i x/L}$  in  $S$  couples only wave functions of symmetry  $k_i$  and  $k_i + 2\pi/L$ . The equivalence of the present formulation with methods based on periodic perturbations [2,4,5,12,13] is then proved for any order of perturbation by induction.

Nunes and Gonze showed for a simple model that their functional admits a region of stability also for *finite* electric fields, but that an instability occurs in the limit of a dense  $k$ -point sampling [12]. In our formulation, the corresponding instability occurs in the limit of large  $L$  ( $L \rightarrow \infty$ ). Indeed, an instability is expected to occur for electric fields  $\mathcal{E}$  larger than  $\sim E_{\text{gap}}/L$ , where  $E_{\text{gap}}$  is the electronic gap.

These considerations allow us to envisage the use of the variational energy functional (1) for treating *finite* homogeneous electric fields in first-principles calculations.

Moreover, this approach can be extended to give atomic forces, and is therefore suitable for implementation in molecular dynamics schemes [14,17]. To this end, we account for the ionic polarization  $P_{\text{ion}}$  by adding the following term to the functional (1):

$$E_{\text{ion}}^\mathcal{E} = -\mathcal{E} \cdot P_{\text{ion}}, \quad \text{where } P_{\text{ion}} = \sum_{i=1}^{N_{\text{ion}}} Z_i \cdot R_i, \quad (8)$$

where  $R_i$  is the position coordinate in the direction of the applied field and  $Z_i$  is the charge of the ionic core. This definition ensures that the force acting on the  $i$ th ion acquires a contribution  $F_i = \mathcal{E} Z_i$ .

We treat finite electric fields by integrating the functional (1) within the widespread scheme based on plane-wave basis sets and pseudopotentials. We use a Car-Parrinello approach [18], in which the coefficients of the wave functions are driven to their ground state by molecular dynamics methods [14]. The expression for the gradients with respect to the wave function's coefficients can be derived along the lines of Ref. [5]. In the case of norm-conserving pseudopotentials, the formal expression of the atomic forces remains unchanged with respect to the case of vanishing field, except for the term  $F_i = \mathcal{E} Z_i$ . We also extended the finite-field formulation to ultrasoft pseudopotentials [19]. In this case, additional terms appear in the expressions of the polarization (2), the gradients with respect to the wave function's coefficients, and the atomic forces [20]. We note that this extension is considerably less involved than the treatment of such pseudopotentials within a perturbational approach [20,21].

To examine the reliability of this approach, we focused on the dielectric properties of bulk MgO. We modeled MgO by a periodic cubic cell containing 64 atoms at the experimental lattice constant. Only valence wave functions were treated explicitly, while core-valence interactions were described by ultrasoft pseudopotentials [19]. The exchange and correlation energy was described by the local density approximation.

First, we investigated the stability of the energy functional (1) as a function of the applied electric field for *fixed* atomic positions. A variational minimum was found for field intensities ranging over several orders of magnitude up to 0.034 atomic units, corresponding to 1.7 V/Å. Beyond this value of the field, the functional could not be minimized. The instability occurs for fields of the same order as the critical field  $E_{\text{gap}}/L = 0.5 \text{ V/Å}$ , where  $L$  is the periodicity of our simulation cell. In Fig. 1, the variation of the polarization  $\Delta P^\mathcal{E} = P^\mathcal{E} - P^0$  shows a close to linear behavior for fields  $\mathcal{E}$  in the range of stability of the energy functional. Within the linear regime, the high-frequency dielectric constant can be estimated from

$$\epsilon_\infty = \frac{4\pi \Delta P^\mathcal{E}}{L^3 \mathcal{E}} + 1, \quad (9)$$

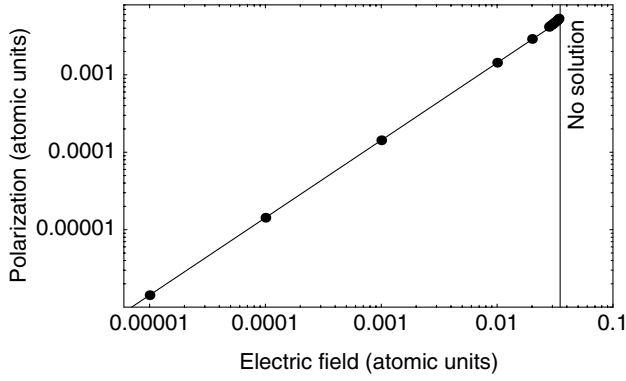


FIG. 1. Calculated polarization per unit volume versus electric field for bulk MgO (disks). The solid line corresponds to the result from linear response [5]. The polarization is given as a difference with respect to the case of vanishing field. For electric fields higher than  $\sim 0.035$  a.u. the functional (1) could not be minimized.

valid for cubic crystals. For a field of  $10^{-3}$  a.u., we found  $\epsilon_\infty = 2.79$ . To check the validity of this result, we generalized the linear response approach of Ref. [5] to treat ultrasoft pseudopotentials [20], and found a numerically equivalent result (within  $10^{-4}$ ). This application illustrates that functional (1) also provides reliable results for *finite*  $\mathcal{E}$ .

The Born effective charges  $Z^*$  are defined as the derivatives of the atomic forces with respect to the applied field [10]. The  $Z^*$  can then be obtained in a straightforward way by using the atomic force  $F^\mathcal{E}$  acting on the ions in the presence of a field  $\mathcal{E}$ :

$$Z^* = \frac{F^\mathcal{E}}{\mathcal{E}}, \quad (10)$$

where we used  $F^{\mathcal{E}=0} = 0$  and the cubic symmetry of the crystal. For a field  $\mathcal{E} = 10^{-3}$  a.u., we obtained  $Z^* = 1.96$ . The charges  $Z^*$  can alternatively be defined as derivatives of the polarization with respect to atomic displacements at vanishing electric field [10]. Using a finite difference approach in which the Mg and O sublattices are relatively displaced by 0.2 bohr, we derived a value of  $Z^* = 1.96$ , numerically coincident with the value obtained with the finite-field method.

To check the validity of the method for describing *atomic relaxations* in a finite electric field, we investigated the static dielectric constant. The difference between the low- and high-frequency dielectric constants is generally expressed in terms of the Born effective charges, the vibrational frequencies, and their associated eigenmodes [22]. For bulk MgO,

$$\Delta\epsilon = \epsilon_0 - \epsilon_\infty = \frac{4\pi (Z^*)^2}{\Omega_0 \mu \omega^2}, \quad (11)$$

where  $\omega$  is the frequency of the zone-center optical phonon,  $\mu$  the reduced mass of Mg and O atoms, and  $\Omega_0$  the

volume of the fcc primitive cell. We obtained the zone-center frequency  $\omega$  by a frozen phonon calculation. Direct application of (11) then gives  $\Delta\epsilon = 5.09$ .

The functional (1) offers an alternative procedure for obtaining static dielectric constants, which entirely avoids the calculation of normal modes. We performed a damped molecular dynamics relaxation, in which the atomic positions are allowed to relax fully in the presence of a finite electric field  $\mathcal{E}$ . In this case,  $\Delta\epsilon$  can be expressed in terms of a difference between polarizations associated with atomic configurations before ( $P_{\text{nonrelaxed}}^\mathcal{E}$ ) and after ( $P_{\text{relaxed}}^\mathcal{E}$ ) atomic relaxation:

$$\Delta\epsilon = \frac{4\pi}{L^3} \frac{P_{\text{relaxed}}^\mathcal{E} - P_{\text{nonrelaxed}}^\mathcal{E}}{\mathcal{E}}, \quad (12)$$

where both polarizations,  $P_{\text{nonrelaxed}}^\mathcal{E}$  and  $P_{\text{relaxed}}^\mathcal{E}$ , are calculated in the presence of a field  $\mathcal{E}$ . In Fig. 2, we plot the evolution of  $\Delta\epsilon$  during the relaxation of the atomic positions in an electric field of  $10^{-3}$  a.u. After a few oscillations,  $\Delta\epsilon$  converges rapidly to 5.14, differing by less than the numerical accuracy from the estimate of 5.09, derived from (11). The dielectric properties obtained for MgO are summarized in Table I, where the experimental results [23] have been included for comparison.

To illustrate the potential of functional (1) for treating complex systems of large size, we considered the dielectric properties of a model structure of vitreous silica [24], for which the Born effective charges [25] and the vibrational properties [26] were obtained previously. Through an electronic relaxation in a field of  $10^{-2}$  a.u., we obtained via (9) a high-frequency dielectric constant of 2.00, in good agreement with the experimental value for vitreous silica ( $\epsilon_\infty^{\text{expt}} = 2.1$  [27]). Applying a linear response method [20], we yielded the same value for  $\epsilon_\infty$ , thereby confirming this result (Table II).

The advantage of using the functional (1) is impressive for the calculation of the Born effective charges and

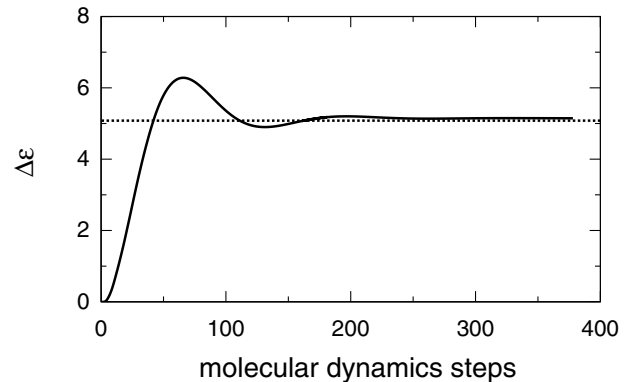


FIG. 2. Evolution of  $\Delta\epsilon$  for a model of MgO during a damped molecular dynamics relaxation in a finite electric field of  $10^{-3}$  a.u. The dotted line corresponds to the result from linear response (11).

TABLE I. Dielectric properties of bulk MgO. We used an electric field  $\mathcal{E}$  of  $10^{-3}$  a.u. The reference values were calculated without finite fields (see text).

	Finite $\mathcal{E}$	Reference	Experiment
$Z^*$	1.96	1.96	1.98
$\epsilon_\infty$	2.79	2.79	2.96
$\epsilon_0$	5.14	5.09	6.67

of the difference  $\Delta\epsilon$  between low- and high-frequency dielectric constants. All the Born effective charges could be obtained via (10) using just three electronic relaxations. This should be contrasted with the method in Ref. [25], which required three electronic relaxations for each atom in the model [28]. The Born effective charges calculated with the two methods are identical within numerical accuracy. Using the molecular dynamics relaxation scheme, we obtained  $\Delta\epsilon$  via (12). We found a value of 1.6, in accord with the result in Ref. [25]. We note that the structural relaxations, required by the finite-field method, imply a substantially smaller computational effort than the calculation of the full dynamical matrix [25,26]. The theoretical value for  $\Delta\epsilon$  (1.6) compares well with the experimental one (1.8).

In conclusion, we introduced a scheme for treating finite electric fields in first-principles calculations. We validated this scheme through comparisons with more established approaches and illustrated its computational efficiency when applied to systems of large size. In particular, we combined the finite-field method with *ab initio* molecular dynamics. This extended scheme offers the possibility of accessing properties which cannot be accessed with any other method currently in use. For instance, the stage is set for following the behavior of a liquid evolving in a homogenous electric field at a given temperature, from both the structural and dielectric points of view.

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TABLE II. High-frequency dielectric constant  $\epsilon_\infty$  and the difference  $\Delta\epsilon$  between low- and high-frequency dielectric constants for a model of vitreous silica [24]. The reference values for  $\epsilon_\infty$  and  $\Delta\epsilon$  are obtained by linear response [5,20] and taken from Ref. [25], respectively. A field  $\mathcal{E}$  of  $10^{-2}$  a.u. was applied along each of the Cartesian directions (see text).

	$\epsilon_\infty$			$\Delta\epsilon$		
	Finite $\mathcal{E}$	Ref.	Expt.	Finite $\mathcal{E}$	Ref.	Expt.
x	1.99	1.99		1.43	1.46	
y	2.01	2.01		1.70	1.67	
z	2.01	2.01		1.56	1.55	
Average	2.00	2.00	2.1	1.56	1.56	1.8

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