Dielectric Response of Periodic Systems from Quantum Monte Carlo Calculations

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We present a novel approach that allows to calculate the dielectric response of periodic systems in the quantum Monte Carlo formalism. We employ a many-body generalization for the electric enthalpy functional, where the coupling with the field is expressed via the Berry-phase formulation for the macroscopic polarization. A self-consistent local Hamiltonian then determines the ground-state wavefunction, allowing for accurate diffusion quantum Monte Carlo calculations where the polarization’s fixed point is estimated from the average on an iterative sequence, sampled via forward-walking. This approach has been validated for the case of an isolated hydrogen atom, and then applied to a periodic system, to calculate the dielectric susceptibility of molecular-hydrogen chains. The results found are in excellent agreement with the best estimates obtained from the extrapolation of quantum-chemistry calculations.

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The response of an extended system to an electric field is an intrinsic property of central importance to the understanding and characterization of bulk materials. First, it depends very sensitively on an accurate description of the correlations between interacting electrons. Second, it allows one to predict observable quantities such as the infrared or (non-resonant) Raman and hyper-Raman spectra, establishing a direct link between macroscopic experimental observations and microscopic calculations. Density-functional approaches to calculate dielectric susceptibilities in periodic systems were introduced more than two decades ago [1, 2, 3, 4]. However, the resulting agreement with experiments is less striking than for the case of structural or vibrational properties, even though the response to a static electric field is strictly a ground-state property [2]. These discrepancies have been related to the intrinsic dependence of the exchange and correlation functional on the polarization [3]: non-local exchange-correlation functionals such as the weighted-density approximation (WDA) [6] also show some improvements upon the local-density (LDA) [2] or generalized-gradient approximations (GGAs) [7]. While in the case of crystalline semiconductors dielectric susceptibilities are usually overestimated by 10 – 30% in LDA or GGAs, linear dielectric susceptibilities of conjugated polymers are usually overestimated by a factor > 2 – 3, and non-linear susceptibilities by orders of magnitude [8, 9, 10]. Linear chains of hydrogen dimers are another clear example of LDA or GGAs failures, and have thus become a stringent test case to assess new developments in density-functional theory [10, 11, 12, 13]. Correlated quantum-chemistry methods are able to predict accurate linear and non-linear polarizabilities for polymeric chains [14], but their less favourable scaling and the need, in the absence of periodic boundary-conditions (PBCs), to extrapolate the results to the infinite system limit their range of applicability.

Highly-accurate ground-state electronic-structure calculations can be performed using continuous quantum Monte Carlo (QMC) methods [15], which benefit from scaling costs as low as $N^{-3}$ [16], where $N$ is the number of electrons. Although diffusion QMC has been successfully applied to address the polarizability of small molecules [17], the extension to bulk materials is hindered by the difficulty in treating the response to a linear electric field, since the latter is non-periodic and incompatible with PBCs. Only the response of the electron gas to a finite wavelength perturbation has been investigated [18]. In density-functional calculations, the response to an electric field has been calculated via its long-wavelength limit using supercells of increasing size [1, 2, 3, 4, 5, 6, 7], or, more elegantly, using linear-response theory [4, 20]. A general approach able to deal with finite fields, and thus both linear and non-linear effects, has also been recently introduced [21, 22]. This method is based on the fact that the macroscopic polarization can be properly defined even in PBCs [23, 24]; then, instead of applying a field in the form a linear potential, a Legendre transform allows one to introduce an electric enthalpy functional whose minimization leads to the correct wavefunctions.

In this work we apply these ideas to the case of correlated electrons, using the many-body formulation of the Berry-phase polarization [25, 26] to deal with the generalization of the electric-enthalpy functional [21, 22, 23, 24] to the interacting case [21]. We show how such an approach can be applied to the case of diffusion quantum Monte Carlo (DMC) calculations, where a local Hamiltonian operator is needed to evolve a population of walkers representing the ground state.

Let’s consider a system of $N$ interacting electrons in a periodic cell of size $L$ (to simplify the notation we describe the one-dimensional case, but the extension to higher dimensions is straightforward). The normalized
many-body wavefunction $\Psi$ obeys PBCs

$$\Psi(x_1, \ldots, x_i + L, \ldots, x_N) = \Psi(x_1, \ldots, x_i, \ldots, x_N).$$

The polarization of the system can be obtained from the single-point Berry phase $[25]$

$$P[\Psi] = -\frac{e}{\Omega} \frac{L}{2\pi} \text{Im} \ln z$$

where $\Omega$ is the size of the cell, $e$ is the electron charge, $G = 2\pi/L$, and $X$ the $N$-body operator

$$X = x_1 + x_2 + \ldots + x_N.$$

The definition of Eq. (2) coincides, in the thermodynamic limit, with the exact many-body observable $[25]$, but it also remains well-defined for any finite $L$. With the many-body polarization well defined, the ground-state wavefunction of a periodic, extended system in the presence of an electric field $\mathcal{E}$ can be obtained from the minimum of the generalized electric enthalpy

$$F[\Psi] = E[\Psi] - \mathcal{E} \delta F[\Psi],$$

where $E[\Psi]$ is the energy functional for the unperturbed Hamiltonian $H^0$. The functional in Eq. (5) could be directly minimized using a variational Monte Carlo approach $[31]$, but it can’t be applied directly to the more accurate case of DMC calculations, since these can only deal with Hamiltonians that are both local and Hermitian. A local Hermitian operator can nevertheless be derived from the minimum condition for the electric enthalpy

$$\frac{\delta F}{\delta \langle\Psi\rangle} = \lambda |\Psi\rangle,$$

with $\lambda$ an appropriate Lagrange multiplier $[33]$. The $\Psi$ that minimizes Eq. (6) is also the ground-state for the many-body self-consistent Hamiltonian

$$H(z) = H^0 + \mathcal{E} \frac{eL}{2\pi} \text{Im} \frac{e^{iG\hat{X}}}{z}$$

where $z$ depends on $\Psi$ through Eq. (4). For any given $L$, there exists a well-defined interval for $\mathcal{E}$ centered around 0 for which the electric enthalpy can be minimized without encountering runaway solutions $[21, 22]$. In addition, all physical observables of interest here (e.g. the linear and nonlinear dielectric susceptibilities) are derivatives of the electric enthalpy with respect to the field and thus remain well-defined for every $L$.

Due to the self-consistent nature of the operator $H(z)$ defined in Eq. (7), the ground state in the presence of an electric field must be found through an iterative procedure. We start from a first value $z_1$ for $z$, e.g. as found in the single-particle calculations or in the many-body trial wave function $\Phi_T$: the local Hamiltonian $H(z_1)$ is then constructed. DMC evolution using this operator leads to a new expectation value for $z$, called $z_2$, which in turn determines a second Hamiltonian $H(z_2)$. In the absence of stochastic noise, this process could be iterated to convergence $z_1 \to z_2 \to z_3 \to \ldots \to z_n$, to find the fixed point of the complex-plane map

$$f(z_i) = z_{i+1}.$$  

Since the Monte Carlo procedure introduces a statistical error in every estimate of $z_i$, the map $f$ becomes a stochastic function in the complex plane. Now, the linear approximation $f(z) = az + b$ is made close to the fixed point of $f(z)$ (linearity will be shown numerically later). Then, the average over a sequence of $\{z_i\}$ provides the estimate for the fixed point $b/(1 - a)$ of $f(z)$, from which the polarization is then obtained via Eq. (2).

This descends straightforwardly from the consideration that $\lim_{N \to \infty} \frac{1}{N} \sum_{i=1}^N z_i$ is the fixed point of the map $f(z)$, since $\frac{1}{N} \sum_{i} z_i = \frac{1}{N} \sum_{i} f(z_{i-1}) = \frac{1}{N} \sum_{i} f(z_i) = \frac{1}{N} \sum_{i} (a z_i + b)$, since the electric enthalpy with respect to the field and thus remain well-defined for every $L$.

| Method     | 10-H$_2$ | 16-H$_2$ | 22-H$_2$ |
|------------|----------|----------|----------|
| DFT-GGA    | 102.0    | 123.4    | 133.5    |
| DMC        | 52.2 $\pm$ 1.3 | 55.4 $\pm$ 1.2 | 53.4 $\pm$ 1.1 |

TABLE I: Linear polarizability per H$_2$ unit for a periodic linear chain of H$_2$ dimers, calculated in PBCs for supercells containing 10, 16, and 22 H$_2$ units.

We use a forward-walking strategy $[35, 36]$ to sample the ex-
determinant of the trial wavefunction $\Phi_T$ were obtained from QUANTUM ESPRESSO [38], using consistently the same finite electric field $\mathcal{E}$ of the QMC calculation [39].

To validate our approach, we first calculate the polarizability of an isolated hydrogen atom, using a large supercell and periodic-boundary conditions. For this case, a homogeneous finite field can be explicitly applied using a saw-tooth potential (i.e. a potential that is both periodic and piecewise linear), and the results compared with those obtained with our method. We use the same GGA trial wavefunctions for both tests, as calculated under an applied electric field of 0.005 a.u. using a local H pseudopotential, 50 Ry cutoff in the plane-wave basis set, and a cell of $20 \times 20 \times 200$ a.u. (the longest direction coincides with the applied electric field, and a large supercell has been used to eliminate finite-size errors [10]). In all DMC calculations we choose a timestep of 0.02 a.u., assuring an acceptance ratio greater than 99.7%. Then, the projection time $\Delta t$ for the forward-walking is determined. We show in Fig. 1(a) the dependence of the expectation value for the polarization of the atom in the absence of an applied field, as a function of the projection time $\Delta t$ in Eq. (9), showing convergence to 0 a.u. for $\Delta t \geq 600$ timesteps. With these parameters, we start our iterative sequence of calculations. The first value for $z$ is taken from the GGA results, and then after each DMC run the local operator $H(z)$ is updated using the current expectation value for $z$. We report in Fig. 1(b) the atomic polarizability calculated from each one of the $z_i$ along the sequence of DMC runs. The average of the $z_i$ over the last 13 runs gives us a fixed point estimate ($0.9995072 \pm 2.5 \times 10^{-7} + 7.05 \times 10^{-4}i \pm 4.0 \times 10^{-6}$) for $f(z)$, and a corresponding polarizability for the H atom of $4.49 \pm 0.03$ a.u., in excellent agreement with the result obtained for the saw-tooth potential ($4.52 \pm 0.05$ a.u.) and the exact value of 4.5 a.u. [41].

Having validated our scheme in an isolated case, we proceed to apply it to a genuine periodic system, namely a linear chain of hydrogen dimers, where standard density-functional theory performs very poorly [10].

We adopt one of the standard geometries reported in the literature [4, 42], where the hydrogen dimers have a H-H bond length of 2.0 a.u. and are separated by 2.5 a.u. . For this case, reliable reference results for the polarizability per dimer unit $\alpha$ are available from correlated quantum-chemistry approaches ($\alpha = 53.6$ a.u. in MP4 and $\alpha = 50.6$ a.u. in CCSD(T)) [42]; these numbers should be contrasted with the PBE-GGA result $\alpha = 144.5$ a.u. [43]. To calculate the DMC susceptibility, we use a trial wavefunction composed of a Slater determinant of PBE-GGA single-particle orbitals (consistently calculated with an electric field of 0.001 a.u.) times a Jastrow term containing the electron-electron and electron-nucleus terms [44]. We consider three supercells containing 10, 16 and 22 H$_2$ units, and the same electric field of 0.001 a.u. . The polarizabilities per unit dimer are found by finite differences (note that the polarization at zero field is zero by symmetry). In Fig. 2(a), we show the polarizability calculated at each DMC run in the 22-unit supercell. After the second iteration, the instantaneous polarizability oscillates roughly around the final value; again, we stress that it is the average of $\{z_i\}$ that delivers the estimate of the fixed point

| Method     | $\alpha$ (a.u.) | Scaling cost |
|------------|-----------------|--------------|
| PBE-GGA    | 144.5           | N-N$^3$      |
| CCD        | 47.6            | N$^2$-N$^6$  |
| CCSD       | 48.0            | N$^6$        |
| CCSD(T)    | 50.6            | N$^7$        |
| MP2        | 58.0            | N$^3$        |
| MP3        | 54.3            | N$^6$        |
| MP4        | 53.6            | N$^7$        |
| DMC        | 53.4±1.1        | N-N$^3$      |

TABLE II: Linear polarizability per H$_2$ unit for a periodic linear chain of H$_2$ dimers calculated using several methods, together with their associated scaling costs. The quantum chemistry results are from Ref. [42].

FIG. 1: (a) Polarization of an isolated H atom in the absence of an electric field as a function of the forward walking parameter $\Delta t$, using a trial wavefunction expressed by a PBE-GGA orbital calculated in the presence of an electric field of 0.005 a.u. . The dashed line is a guide to the eye. (b) Polarizability of an isolated H atom, for each of the self-consistent DMC runs in the iterative sequence (see text). The dashed line is a guide to the eye.

FIG. 2: (a) Linear polarizability per H$_2$ unit for a periodic linear chain of 22 H$_2$ dimers in PBCs, for each of the self-consistent DMC runs in the iterative sequence (see text). The dashed line is a guide to the eye. (b) Last ten $z_i$ values (thin), and estimate of the fixed point of $f(z)$ (bold).
and thus the final polarization. In Fig. 2(b), we show the distribution of the last ten $z_i$, and the fixed point \( (0.8029 \pm 4.1 \times 10^{-4}, 6.0 \times 10^{-2} \pm 1.1 \times 10^{-3}) \), obtained from their average. In Table II we illustrate the convergence of the calculated polarizability with respect to the supercell size. The faster convergence with respect to the PBE-GGA case originates in the stronger localization of $\Psi$ in DMC. Indeed, the localization spread of $\langle L_z^2 \rangle$ decreases from 4.32 a.u. (i.e., Bohr$^2$) for PBE-GGA to 2.44 $\pm$ 0.01 a.u. in DMC for the 22 units supercell. Finally, we compare in Table II our final result $\alpha = 53.4 \pm 1.1$ a.u. with those obtained using other approaches: we find excellent agreement with the most accurate results available using MP3 and MP4. We note in passing that the correlated quantum chemistry polarizabilities have been extrapolated from calculations performed for finite chains \([12]\), with the extrapolative correction amounting to 20% of the final results.

In conclusion, we introduced and validated a novel approach to study periodic systems in the presence of finite electric-fields with highly-accurate, and in principle linear-scaling, diffusion QMC calculations. In particular, we presented the first QMC evaluation of the linear dielectric susceptibility of an extended system. For the paradigmatic test case of hydrogen chains, we obtained excellent agreement with the best quantum-chemistry results. Our approach opens the possibility to evaluate linear and nonlinear dielectric properties, effective charges, and Raman and infrared coupling tensors using QMC calculations.

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[44] These terms in the Jastrow factor are spherically symmetric in the present implementation. Thus, the addition and optimization of the Jastrow factor to a Slater determinant of polarized PBE-GGA orbitals shows only a marginal improvement (around 5% for the hydrogen chain) for the expectation value of the polarization.

[45] The DMC results were obtained from z-averages over 10 – 11 runs, each of them with 256000 time-steps and an average population of 1000 walkers. We verified linearity in the complex map, by repeating the calculation for 10 – H2 using 29 runs of 64000 timesteps, obtaining 53.0 ± 1.4 a.u. .

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