Linear and Non-linear Susceptibilities from Diffusion Quantum Monte Carlo: Application to Periodic Hydrogen Chains

P. Umari,1,2 and Nicola Marzari2
1CNR-INFM Democritos, Theory@Elettra Group, Basovizza, Trieste, Italy and
2Department of Materials Science and Engineering, MIT, 02139 Cambridge MA
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We calculate the linear and non-linear susceptibilities of periodic longitudinal chains of hydrogen dimers with different bond-length alternations using a diffusion quantum Monte Carlo approach. These quantities are derived from the changes in electronic polarization as a function of applied finite electric field - an approach we recently introduced and made possible by the use of a Berry-phase, many-body electric-enthalpy functional. Calculated susceptibilities and hyper-susceptibilities are found to be in excellent agreement with the best estimates available from quantum chemistry - usually extrapolations to the infinite-chain limit of calculations for chains of finite length. It is found that while exchange effects dominate the proper description of the susceptibilities, second hyper-susceptibilities are greatly affected by electronic correlations. We also assess how different approximations to the nodal surface of the many-body wavefunction affect the accuracy of the calculated susceptibilities.

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I. INTRODUCTION

The linear and non-linear longitudinal dielectric susceptibilities of periodic linear chains of hydrogen dimers have been in recent years the subject of many density-functional theory and quantum chemistry studies [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. When dielectric properties are considered, these model systems present appealing similarities with real polymeric chains. In particular, in both systems the second hyper-susceptibilities are very large. Despite the apparent simplicity of such systems, obtaining reliable results for susceptibilities and hyper-susceptibilities requires particular care [14]. Density-functional theory approaches using the local density (LDA) or generalized-gradient (GGA) approximations strongly overestimate dielectric response, up to several orders of magnitude in the case of the second hyper-susceptibility, and more sophisticated approaches need to be considered [13]. Correlated quantum chemistry approaches, such as Møller-Plesset (MP) and coupled-cluster (CC), provide benchmark results, although carefully converged results often require the most sophisticated levels of approximations (MP4,CCSD(T)) and extended basis sets [2].

Recently, we have introduced a novel scheme for the treatment of finite static homogeneous electric fields in periodic quantum Monte Carlo (QMC) calculations [10]. The use of periodic boundary conditions (PBCs) permits to avoid the extrapolations to the infinite chain limit, which would be even more cumbersome in this case due to the presence of QMC statistical errors. When applied to the hydrogen chain model, this approach provides linear susceptibilities in excellent agreement with the results from the most accurate quantum chemistry calculations. Since it has been shown that, in contrast to the linear response case, electronic correlations account for a large extent to second hyper-susceptibilities [2], it is of particular interest to assess the accuracy and reliability of QMC for the calculation of these higher-order responses. Indeed in QMC, in the limit of a correct nodal surface approximation, electronic correlations are treated exactly and basis sets approximations are easily controlled. Moreover, due to the favorable scaling of QMC approaches with respect to the number of electrons (cubic, or even linear [17]), this approach could represent a very viable strategy for accurate, predictive calculations of non-linear dielectric properties in realistic systems.

Here, we calculate with diffusion quantum Monte Carlo (DMC) the linear polarizability and second hyper-polarizability per H2 unit (i.e. the susceptibilities) for the paradigmatic case of periodic linear chains of hydrogen dimers, where the dimers have a fixed length of 2.0 a. u. and we consider three different bond-length alternations of 2.5 a. u. 3.0 a. u. and 4.0 a. u. respectively.

The paper is organized as follows: Section III briefly describes our methodology to treat finite electric fields in periodic QMC calculations. In Section III we summarize the technical details of the calculations and investigate the degree of convergence with respect to the different approximations used. The final results are reported and discussed in Section IV while in Section V we investigate the errors induced by different choices for the many-body nodal surface. Conclusions, and perspectives for future work are drawn in Section VI.

II. METHOD

We briefly summarize here the approach we first introduced in Ref. [10]. We consider a system of N interacting electrons in a periodic cell of size L (to simplify the notation we describe here the one-dimensional case, but the extension to higher dimensions is straightforward). The
normalized many-body wavefunction $\Psi$ obeys PBCs

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

(1)

for every $i$. On the other hand, the position operator

$$\hat{X} = x_1 + x_2 + \ldots + x_N,$$

(2)
does not satisfy PBCs and is unbounded from below; thus it cannot be used (and would be ill-defined) to calculate expectation values, say, of the potential generated by a constant electric field. On the other hand, the modern theory of the polarization of density functional theory in Refs. [22, 23]. On the enthalpy functional has been firstly introduced for tight-binding Hamiltonian [21] and its many-body generalization [22, 23] provide definitions for the relevant observables which remains compatible with PBCs. Indeed, the polarization $P$ of a many-body system can be obtained from the single-point Berry phase formulation

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

(3)

$$z[\Psi] = \langle \Psi | e^{iG\hat{X}} | \Psi \rangle,$$

(4)

where $\Omega$ is the size of the cell (in 1d is equal to $L$), $e$ is the elementary charge, $G = 2\pi/L$, and $z$ will be termed here as the complex polarization. The definition of Eq. (3) coincides, in the thermodynamic limit, with the exact many-body observable [21], but it remains well-defined for any finite $L$. Although in Eq. (3) the polarization is defined modulo $-eL/\Omega$, the quantities which are experimentally observed correspond to differences of polarization and are well defined within the MTP.

Having a valid definition for the many-body polarization, we can operate a Legendre transform of our total energy functional between the conjugate variables of electric field $E$ and polarization $P$, and obtain the ground-state wavefunction of a periodic, extended system in the presence of an electric field $E$ from the minimum of the generalized electric enthalpy [22, 23, 24, 25, 26]

$$F[\Psi] = E^0[\Psi] - E\Omega P[\Psi],$$

(5)

where $E^0[\Psi]$ is the energy functional for the unperturbed Hamiltonian $H^0$. The direct minimization of an electric enthalpy functional has been firstly introduced for tight-binding Hamiltonians in Ref. [24] and in the context of density functional theory in Refs. [22, 23]. On the other hand, DMC and variational Monte Carlo (VMC) (with variance minimization approaches) require the use of Hamiltonian operators which are both local and Hermitian. This requirement can be satisfied by noting that a local Hermitian operator can be identified from the minimum condition for the electric enthalpy

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

(6)

with $\lambda$ the appropriate Lagrange multiplier. This strategy has already been used for the case of single-particle Slater determinants [27] and model Hubbard Hamiltonians [26]. This local Hermitian operator shares the same ground-state wavefunction of the electric enthalpy functional, and the $\Psi$ that minimizes Eq. (5) is also the ground-state for the many-body Hamiltonian

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

(7)

It should be noted that Eq. (7) defines a self-consistent many-body Hamiltonian, since it’s an operator that depends on the complex polarization $z$, and thus on the expectation value of $\Psi$ through Eq. (4). Self-consistency is indeed the price to be paid to recast the variational principles of the electric-enthalpy functional into an operator equation.

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 $\Psi_T$: 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:

$$z_1 \rightarrow z_2 \rightarrow z_3 \rightarrow \ldots \rightarrow z_n,$$

(8)

to find the fixed point of the complex-plane map

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

(9)

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. If $f$ can be approximated close to its fixed point as a linear function in the complex plane, it has been shown [16, 17] that its average over a sequence of $\{z_i\}$ provides the best estimate for the fixed point itself. The validity of this approximation must be checked numerically. Once the fixed point $\bar{z}$ is obtained, the corresponding polarization is then obtained via Eq. (4).

### III. COMPUTATIONAL DETAILS

We investigate in this study dielectric properties of periodic linear chains of hydrogen dimers along the longi-
tudinal direction. The chosen dimer bond length is 2.0 a. u. and bond-length alternations of 2.5, 3.0 and 4.0 a. u. are considered. Because of symmetry, these systems have vanishing first hyper-susceptibility. We treat these systems through periodic boundary conditions. We first perform HF calculations using an orthonormal unit cell with an edge size of 20 a. u. in the directions perpendicular to the chain and containing one single H$_2$ unit. We sample the one-dimensional Brillouin zone along the
chain direction with a set of $N_k$ equally spaced k-points. Then, for QMC calculations the corresponding supercell containing $N_k$ hydrogen dimers, sampled at the Γ-point, is considered. The HF calculations are performed using the PWSCE package from the QUANTUM-ESPRESSO distribution. The wave-functions are expanded in a plane-wave basis set with a cutoff of 50 Ry. Finite electric fields are implemented through the algorithm described in Ref. [27]. To describe the Coulomb potential of the H nucleus we use a norm-conserving pseudopotential. For this same pseudopotential we already showed in Ref. [10] that the calculated DMC polarizability of the isolated H atom is in perfect agreement with the theoretical value.

The convergence of the Berry-phase polarization to the thermodynamic limit is of the order $L^{-2}$ with respect to the supercell dimension $L$; this can be understood on purely geometrical grounds (see Ref. [26]). Thus, we determine here the k-point sampling $N_k$ for the primitive unit cell, and equivalently the length of a supercell sampled at the Γ point, for which the sampling/geometrical errors in the calculated linear susceptibility and second hyper-susceptibility become smaller or negligible with respect to the magnitude of the statistical errors due to the DMC procedure. We investigate this convergence within the HF approach, focusing on chains with a bond-length alternations of 3 a. u., for which also extrapolations to the infinite chain limit for both the polarizability and hyper-polarizability have been reported for several basis sets in Ref. [2]. We consider two values for $N_k$, 10 and 20, and use two applied electric fields of magnitude 0.003 and 0.02 a. u. respectively. We then fit the dipole moment $\mu$ per H$_2$ unit with

$$\mu(\mathcal{E}) = \alpha\mathcal{E} + \frac{1}{6}\gamma\mathcal{E}^3,$$

(10)

where $\mathcal{E}$ is the electric field and $\alpha$ and $\gamma$ are the linear susceptibility and the second hyper-susceptibility per H$_2$ unit. We report in Tab. II the values for $\alpha$ and $\gamma$ we calculated using PBCs, together with the extrapolations for the most complete basis sets presented in Refs. 1,2, showing very good agreement with these published calculations. As we want to focus here on the non-linear susceptibility we will consider in the following supercells of 10 dimers each, i.e. corresponding to $N_k = 10$ sampling.

The calculated HF wavefunctions are then interpolated with splines and imported into the CASINO VMC and DMC codes [30]. In VMC the N-body wavefunction $\Psi_{\text{VMC}}$ is defined as

$$\Psi_{\text{VMC}}(r_1, ..., r_N) = \exp(J(r_1, ..., r_N)) \frac{1}{\sqrt{N!}} \det(\psi_1 ... \psi_N),$$

(11)

where $\{r\}$ are the electron positions, $\{\psi\}$ are the HF single-electron wavefunctions and $J$ is the Jastrow factor. In this work we use the Jastrow factor formulation introduced in Ref. [31], which depends only on the distances $|r_i - r_j|$ and $|r_i - R_{ij}|$, where $\{R\}$ are the ionic positions. We use an expansion to the sixth order for both spin components, and two different sets of parameters for inequivalent H ions. Indeed, when a longitudinal field is applied, the two H atoms in the unit cell are no longer equivalent. To optimize the Jastrow parameters we apply a variance minimization scheme [34]. For VMC simulations we adjust the time-step in order to assure an acceptance ratio of $n-50\%$. It should be noted that we use a spherical symmetrical Jastrow factor that depends only on the relative distance between electrons and between electrons and nuclei. Such form does not allow, in the VMC procedure, for significant changes of the expectation value of $z$ (defined in Eq. (3)) with respect to its original HF value. Moreover, the variance minimization scheme used here is less sensitive to long range properties than energy minimization schemes [32, 33].

In the following, we consider a hydrogen chain with a bond-length alternation of 2.5 a. u., as done in Ref. [16]. We report in Tab. III the estimates for the total electric enthalpy and $z$ complex polarization obtained in the presence of an electric field of 0.003 a. u. and for several consecutive steps of the Jastrow factor optimization. As expected, we note a significant lowering of the total electric enthalpy due to the $E^3$ term in Eq. (3), while the polarization remains almost unchanged.

Once the Jastrow factor has been optimized, the resulting N-body wavefunction $\Psi_{\text{VMC}}$ is used as trial wavefunction for the DMC simulations, which are based on importance sampling. In all the DMC calculations we use a time step of 0.02 a. u. assuring an acceptance ratio greater than 99.7%. Indeed, in the DMC simulations the walkers are distributed as $\Psi_{\text{VMC}}\Psi$, where $\Psi$ is the correct N-body ground-state wavefunction compatible with the nodal surface defined by $\Psi_{\text{VMC}}$. The expectation value $\bar{O}$ of an operator $O$ which does not commute with the Hamiltonian and depends only on the electron positions $\{r\}$ is obtained through a forward-walking procedure [35, 36]

$$\bar{O} = \sum_{\tau} \sum_{j = 1, N_v} O(\{r_j, \tau - \Delta t\}) \frac{1}{\sum_{\tau} N_v},$$

(12)

where $N_v$ is the number of walkers at time-step $\tau$ and $r_j, \tau - \Delta t$ corresponds to the ancestor configuration of the walker $j$ at an interval $\Delta t$ back in imaginary time. To determine the projection time $\Delta t$ we start from a $\Psi_{\text{VMC}}$ calculated for an electric field of 0.003 a. u. and switch off the electric field $\mathcal{E}$ in the following DMC simulation. Then we calculate the expectation values of $z$ for increasing values of $\Delta t$ and through Eq. (3) the corresponding dipole moments. These are expected to decay exponentially toward a small value. Indeed constraining $\Psi$ to the nodal surface of $\Psi_{\text{VMC}}$, which is calculated for a non-zero electric field, prevents the complete relaxation of the dipole moment when the field is switched off in the DMC simulation. In Tab. III we display the decay of the dipole moment for $\Delta t$ ranging from 0 to 1000 time steps. In this study we then use a $\Delta t$ corresponding to 1000 time steps which assures the convergence of the estimated values of $z$ with respect to the statistical errors of our DMC simu-
lations. We do not report in the calculated DMC errors the residual bias due to the use of the finite projection time $\Delta$.

Last, to verify the linearity of the map $f$ in Eq. (9) in the vicinity of its fixed point we perform two different sequences of DMC simulations, as described in Eq. [8], starting with the $z$ value given by HF in an applied electric field of 0.003 a. u. . While both series have a population of 2560 walkers, the first one is composed of 20 DMC simulations of 40000 time steps each, while the second one is composed of 6 DMC simulations of 120000 time steps each. Therefore, larger error bars for each estimate $z$ are found in the first series. We expect that if $f$ is linear the calculated average values $\overline{z}$ should be the same for the first and second series, within the statistical error. Indeed, we report in Tab. IV the average $\overline{z}$ together with the corresponding dipole moments found for the two series. Both quantities are found to be equal within the statistical errors. Thus, in the following DMC simulations we use runs of 40000 time steps each and with a population of 2560 walkers.

**IV. RESULTS AND DISCUSSION**

Using the computational scheme and optimal parameters described in the previous sections we consider linear hydrogen chains with bond-length alternations of 2.5, 3.0 and 4.0 a. u., intermolecular distances of 2.0 a. u. described with 10-dimer supercells in PBCs, to calculate the DMC best estimates for the fixed-point $\overline{z}$ at two different values of the applied electric field. We report in Tab. V these estimates $\overline{z}$ for the complex polarization, together with the corresponding dipole moments per $\text{H}_2$ unit. Since these systems are centro-symmetric, we consider the dipole moment to be zero in the absence an electric field. For larger bond-length alternations it is possible to access larger field intensities without runaway solutions in the HF calculations.

Then, we fit the calculated moments with the expansion of Eq. (10), and obtain the DMC estimates for the linear susceptibility $\alpha$ and second hyper-susceptibility $\gamma$. The linear susceptibilities are reported in Tab. VI together with the quantum chemistry extrapolations of Ref. [1]. We determine $\alpha$ with statistical errors varying from 1.5 % to 0.4 % for the 3.0 a. u. and 4.0 a. u. bond-length alternations, respectively. The higher precision in the latter case is due to the application of higher electric fields. The reported Møller-Plesset susceptibilities calculated for the levels of approximation MP3 and MP4 and for the (6)-31G(*)* and (6)-311G(*)* basis sets show a good degree of convergence with the level of approximation (from MP3 to MP4) and a slightly worse degree of convergence when using a more complete basis set (from (6)-31G(*)* to (6)-311G(*)*). Similar results to the MP4 case are obtained using the coupled cluster CCSD(T) method, as illustrated in Ref. [1]. Our DMC estimates for $\alpha$ are in excellent agreement with the MP4 values calculated for the basis set (6)-311G(*)*. In Ref. [10], the same good agreement was found for the chain with a bond-length alternation of 2.5 a. u. and using a trial wavefunction obtained from a density-functional calculation.

We show in Tab. VII the calculated DMC estimates for the second hyper-susceptibility $\gamma$, together with the quantum chemistry extrapolations of Ref. [2]. We determine $\gamma$ with statistical errors varying from 6.8 % to 3.6 % for the 3.0 a. u. and 4.0 a. u. bond-length alternations, respectively. Values from MP quantum chemistry extrapolations are available only for the 3.0 a. u. bond-length alternation case. These show slow convergence in the MP series (MP3 to MP4) and are still not converged with the basis set (from (6)-31G(*)* to (6)-311G(*)*). However, in Ref. [2] it has been shown that $\gamma$ calculated through MP3 and MP4 increases while the basis set is becoming more complete. Therefore, the best MP4 value should be taken as a lower limit. In fact, the $\gamma$ coefficient calculated through DMC is found to be higher than the MP4 counterpart by a factor of $\sim$20%.

By addressing the difference between the susceptibilities calculated with HF and those calculated with DMC, we can investigate the relevance of electronic correlations. We report in Tab. VIII these differences with respect to the corresponding DMC susceptibilities and hyper-susceptibilities. Electronic correlations lower the value of linear susceptibilities $\alpha$ and increase that of second hyper-susceptibilities $\gamma$. As already shown in Ref. [2], the effects of correlations are large for the second hyper-susceptibility $\gamma$. Indeed, they account for almost half of the calculated DMC value for the chain with a bond-length alternation of 2.5 a. u. . As the bond-length alternation increases the correlation contribution becomes smaller but still remains considerable. Therefore, when calculating non-linear susceptibilities in such systems, an adequate treatment of electronic correlations is mandatory and QMC approaches are particularly appealing since in the limit of the exact nodal surface they treat correlations exactly.

It is worth investigating the localization of the $N$-body wavefunction $\Psi$ along the longitudinal chain direction. The MTP provides a definition of the localization spread $\sigma^2$ which remain valid also within PBCs. This depends solely on the complex number $\overline{z}$ which we estimated in DMC, and the following holds

$$\sigma^2 = \frac{L^2}{N^4 \pi^2} \ln |\overline{z}|^2.$$  (13)

We report in Tab. IX the DMC spreads $\sigma^2$ for the bond-length alternations and electric fields addressed. We note that as the bond-length alternation increases the system becomes more localized. Indeed in the limit of large bond-length alternations, the system becomes composed of isolated hydrogen dimers. The opposite behavior is observed when the electric field is increased. Indeed an applied electric field closes the electronic gap, and this
determines an increase of the electronic spread as shown in Ref. [38].

Finally, we address the converge of the calculated DMC linear susceptibilities and second-hyper susceptibilities with respect to the size of the supercell used in the simulation. We consider a bond length alternation of 4 a.u. and we perform an additional calculation for a supercell consisting of 20 H\textsubscript{2} units. We use the same calculation parameters of the previous DMC simulations. We see from the figures reported in Tab. XI that, in the limit of the statistical error, many-body effects play a minor role. However, a full assessment of the convergence of the second-hyper susceptibility with respect to the supercell size would require significant smaller error-bars.

V. NODAL SURFACE APPROXIMATION

In this section we address the dependence of the calculated DMC dipole moments with respect to the nodal surface through the choice of the trial wavefunction. To estimate the magnitude of the error due to an approximate nodal surface, we consider the hydrogen chain with a bond-length alternation of 2.5 a.u. and proceed in this way: first we calculate HF trial wave-functions applying electric field intensities of 0.0, 0.003 and 0.01 a.u. then, the following VMC and DMC simulations are performed for an electric field of 0.003 a.u. and the fixed points \( \tau \) and dipole moments are compared. The discrepancies between the DMC values calculated starting from HF wavefunctions obtained consistently for an electric field intensity of 0.003 a.u. and those from wavefunctions obtained at fields of 0. and 0.01 a.u. are due to the different nodal surfaces. These values are displayed in Tab. XI together with the corresponding dipole moments. We note that for our system the imaginary part of \( \tau \) is most affected by the choice of the starting trial wavefunction. As expected, the dipole moment is found to be smaller when starting from an HF wavefunction presenting a smaller dipole moment and becomes larger when the HF wavefunction has a larger one. However, this discrepancy is not very large: when starting from LDA trial wavefunctions, which strongly overestimate the linear susceptibilities, the DMC linear susceptibility was still in excellent agreement with the best quantum chemistry results. This could be due to the resemblance with genuine one dimensional systems for which the nodal surface is fixed by symmetry.

VI. CONCLUSIONS AND PERSPECTIVES

We have shown how it is possible to calculate linear and non-linear susceptibilities of periodic systems using DMC, obtaining for the cases studied statistical errors lower than 1.5% for the linear susceptibilities and 7% for the non-linear susceptibilities. The calculated values are in excellent agreement (when available) with the results obtained from the most accurate quantum chemistry approaches, but do not suffer from basis set errors or extrapolations to the infinite limit. These results and approach can be expected to be used as reference for testing novel first-principles approaches for the evaluation of dielectrics properties. Although DMC calculations of susceptibilities are computational demanding, they can benefit, in terms of computational speed, from the use of order-N methods based on localized orthogonal [17, 39] or nonorthogonal basis sets [40, 41]. Therefore, it would be of great interest to determine the accuracy of the calculated dielectric properties when such approximations are used. DMC estimates of linear and non-linear dielectric properties could be particularly important for systems for which less expensive approaches, such as density-functional theory, fail. Polymers and conjugated organic molecules are a prototypical class of these systems, of great theoretical and practical interest.

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\[ N_k = 10 \quad N_k = 20 \quad (6)-31G(*)* \quad (6)-311G(*)* \]

\[ \begin{array}{cccc}
\alpha & 28.5 & 28.5 & 28.5 & 28.6 \\
\gamma & 56.0 & 57.1 & 55.1 & 56.7 \\
\end{array} \]

| \#VMC run | \( F \) | \( \Re\{z\} \) | \( \Im\{z\} \) |
|----------|------|--------|--------|
| 0        | -10.6855 ± 0.0011 | 0.6118 ± 0.0004 | 0.1443 ± 0.0004 |
| 1        | -11.1162 ± 0.0015 | 0.6128 ± 0.0013 | 0.1453 ± 0.0013 |
| 2        | -11.1608 ± 0.0014 | 0.6128 ± 0.0014 | 0.1472 ± 0.0014 |
| 3        | -11.1582 ± 0.0014 | 0.6141 ± 0.0014 | 0.1466 ± 0.0014 |

| \( \Delta t \) (time steps) | \( \mu \) (a. u.) |
|-----------------------------|------------------|
| 0                           | 30.8 ± 1.3       |
| 100                         | 22.8 ± 1.4       |
| 200                         | 17.6 ± 1.5       |
| 300                         | 13.9 ± 1.6       |
| 400                         | 11.2 ± 1.7       |
| 500                         | 9.2 ± 1.8        |
| 600                         | 7.8 ± 2.0        |
| 700                         | 6.8 ± 2.1        |
| 800                         | 6.1 ± 2.3        |
| 900                         | 5.6 ± 2.4        |
| 1000                        | 5.4 ± 2.6        |

TABLE I: Hartree-Fock linear susceptibility \( \alpha \) in a. u. per \( \text{H}_2 \) unit and second hyper-susceptibility \( \gamma \) in \( 10^3 \) a. u. per \( \text{H}_2 \) unit for the periodic linear chain of \( \text{H}_2 \) dimers \( (d=2.0 \text{ a. u.}) \) with a bond-length alternation of 3 a. u., calculated using PBCs and meshes of \( N_k = 10 \) and \( N_k = 20 \) equally spaced \( k \)-points. The quantum chemistry extrapolations to the infinite limit, obtained with basis sets \( (6)-31G(*)* \) and \( (6)-311G(*)* \), are taken from Refs. [1, 2].

TABLE II: Electric enthalpy \( F \) and complex polarization \( z \) obtained in 4 consecutive VMC runs for a periodic hydrogen linear chain of \( \text{H}_2 \) dimers \( (d=2.0 \text{ a. u.}) \) with a bond-length alternation of 2.5 a. u. and an applied electric field of 0.003 a. u. The supercell contains 10 dimers. In the 0-th run no Jastrow term is used and the simulation has a population of \( 3.2*10^6 \) walkers. In runs 1-3 the Jastrow factor is optimized starting from the parameters used in Ref. [16], and the simulations have a population of \( 3.2*10^5 \) walkers.

TABLE III: DMC dipole moment \( \mu \) per \( \text{H}_2 \) unit for a linear periodic chain (10-dimer supercell) with a bond-length alternation of 2.5 a. u., as a function of the forward-walking projection time \( \Delta t \). The VMC trial wavefunction used has been determined with an applied electric field of 0.003 a. u. No electric field is applied during the DMC simulations, each involving 1000 walkers and 36000 time steps.
# time-steps # runs \( \Re\{z\} \) \( \Im\{z\} \) \( \mu \) (a. u.)
\hline
40000 & 20 & 0.6122 \pm 0.0007 & 0.1345 \pm 0.0016 & 0.1549 \pm 0.0020 \\
120000 & 6 & 0.6130 \pm 0.0008 & 0.1334 \pm 0.0015 & 0.1545 \pm 0.0018 \\
\hline

TABLE IV: Real and imaginary part of the estimated fixed point \( z \) for the complex polarization and corresponding dipole moment \( \mu \) per \( \text{H}_2 \) unit, calculated for a linear periodic chain (10-dimer supercell) with a bond-length alternation of 2.5 a. u. and an applied electric field of 0.003 a. u., for two iterative series with (# time-steps) time-steps per single run, and (# runs) total number of DMC runs.

\[ L \text{(a. u.)} \quad \mathcal{E} \text{(a. u.)} \quad \Re\{\tau\} \quad \Im\{\tau\} \quad \mu \text{(a. u.)} \]
\hline
2.5 & 0.003 & 0.6127 \pm 0.0008 & 0.1341 \pm 0.0013 & 0.1544 \pm 0.0018 \\
2.5 & 0.01 & 0.3736 \pm 0.0020 & 0.4320 \pm 0.0034 & 0.6143 \pm 0.0050 \\
3.0 & 0.003 & 0.7544 \pm 0.0005 & 0.0775 \pm 0.0013 & 0.0815 \pm 0.0015 \\
3.0 & 0.02 & 0.4724 \pm 0.0040 & 0.5162 \pm 0.0021 & 0.6602 \pm 0.0053 \\
4.0 & 0.01 & 0.8460 \pm 0.0002 & 0.1459 \pm 0.0008 & 0.1631 \pm 0.0010 \\
4.0 & 0.03 & 0.6996 \pm 0.0008 & 0.4600 \pm 0.0013 & 0.5554 \pm 0.0016 \\
\hline

TABLE V: Real and imaginary part of the estimated fixed point \( z \) for the complex polarization, and corresponding dipole moment \( \mu \) per \( \text{H}_2 \) unit, for periodic hydrogen chains with bond-length alternation \( L \) and applied electric field \( \mathcal{E} \).

\[ L \text{(a. u.)} \quad \text{DMC} \quad \text{MP3(a)} \quad \text{MP3(b)} \quad \text{MP4(a)} \quad \text{MP4(b)} \]
\hline
2.5 & 50.57 \pm 0.50 & 51.35 & 54.33 & 50.02 & 53.56 \\
3.0 & 27.03 \pm 0.55 & 25.66 & 27.01 & 24.94 & 26.51 \\
4.0 & 16.04 \pm 0.10 & 15.4 & 16.13 & 15.00 & 15.83 \\
\hline

TABLE VI: DMC linear susceptibility \( \alpha \) in a. u. per \( \text{H}_2 \) unit for periodic linear hydrogen chains with bond-length alternation \( L \), compared with quantum chemistry results from Ref. [1] reported for the basis set (6)-31G(*)* (a) and (6)-311G(*)* (b).

\[ L \text{(a. u.)} \quad \text{DMC} \quad \text{MP3(a)} \quad \text{MP3(b)} \quad \text{MP4(a)} \quad \text{MP4(b)} \]
\hline
2.5 & 652. \pm 61. \\
3.0 & 89.8 \pm 12. & 65.73 \pm 0.06 & 73.00 \pm 0.05 & 65.77 \pm 0.11 & 74.68 \pm 0.05 \\
4.0 & 16.5 \pm 1.1 \\
\hline

TABLE VII: DMC second hyper-susceptibility \( \gamma \) in units of \( 10^3 \) a. u. per \( \text{H}_2 \) unit for periodic linear hydrogen chains with bond-length alternation \( L \); for the chain with \( L=3.0 \) a. u., quantum chemistry MP results are taken from Ref. [2], and are reported for the basis sets (6)-31G(*)* (a) and (6)-311G(*)* (b).

\[ L \text{(a. u.)} \quad \text{Difference} \quad \text{Relative Difference} \]
\hline
2.5 & -3.69 & 260.70 & -7.3 & 40. \\
3.0 & -1.47 & 33.8 & -5.4 & 37. \\
4.0 & -1.35 & 3.63 & -8.4 & 22. \\
\hline

TABLE VIII: Differences between DMC and HF values for the linear susceptibility \( \alpha \) in a. u. per \( \text{H}_2 \) unit and for the second hyper-susceptibility \( \gamma \) in \( 10^3 \) a. u. per \( \text{H}_2 \) unit and relative differences in percent, for hydrogen chains with bond-length alternations \( L \).
 TABLE IX: DMC localization $\sigma^2$ along the longitudinal direction of hydrogen chains with bond-length alternations $L$ for electric fields $E$.

| $L$ (a. u.) | $E$ (a. u.) | $\sigma^2$ (a. u.) |
|------------|-------------|-------------------|
| 2.5        | 0.003       | 2.396 ± 0.009     |
| 2.5        | 0.01        | 2.873 ± 0.035     |
| 3.0        | 0.003       | 1.751 ± 0.005     |
| 3.0        | 0.01        | 2.261 ± 0.040     |
| 4.0        | 0.01        | 1.391 ± 0.003     |
| 4.0        | 0.03        | 1.620 ± 0.014     |

TABLE X: DMC linear susceptibility $\alpha$ in a. u. and second hyper-susceptibility $\gamma$ in units of $10^3$ a. u. per H$_2$ unit for periodic linear hydrogen chains with bond-length alternation $L=4.0$ a. u. calculated with supercells containing $N$ H$_2$ units.

| $N$ | $\alpha$ (a. u.) | $\gamma$ (a. u.) |
|-----|-------------------|-------------------|
| 10   | 16.04 ± 0.10      | 16.5 ± 1.1        |
| 20   | 15.70 ± 0.17      | 12.7 ± 2.9        |

TABLE XI: Longitudinal dipole moment $\mu$ and fixed point $\overline{z}$ calculated through DMC and HF for an hydrogen chain with bond-length alternation of 2.5 a. u. and for an electric field of 0.003 a. u. The trial wavefunctions are obtained from HF calculations with electric fields $E$.

| $E$ (a. u.) | $\Re\{\overline{z}_{\text{DMC}}\}$ | $\Im\{\overline{z}_{\text{DMC}}\}$ | $\mu_{\text{DMC}}$ (a. u.) | $\Re\{\overline{z}_{\text{HF}}\}$ | $\Im\{\overline{z}_{\text{HF}}\}$ | $\mu_{\text{HF}}$ (a. u.) |
|------------|-----------------------------------|-----------------------------------|----------------------------|-----------------------------------|-----------------------------------|----------------------------|
| 0          | 0.6146 ± 0.0011                   | 0.1249 ± 0.0019                   | 0.1436 ± 0.0019             | 0.6311                            | 0.0000                            | 0.                         |
| 0.003      | 0.6127 ± 0.0008                   | 0.1341 ± 0.0013                   | 0.1544 ± 0.0018             | 0.6118                            | 0.1443                            | 0.1654                     |
| 0.01       | 0.6102 ± 0.0011                   | 0.1608 ± 0.0024                   | 0.1846 ± 0.0029             | 0.4021                            | 0.4536                            | 0.6055                     |