Computational protocol to evaluate electron-phonon interactions within density matrix perturbation theory

Han Yang,†‡ Marco Govoni,*,¶† Arpan Kundu,† and Giulia Galli*,†‡¶

†Department of Chemistry, University of Chicago, Chicago, Illinois 60637, United States
‡Pritzker School of Molecular Engineering, The University of Chicago, Chicago, Illinois 60637, United States
¶Materials Science Division and Center for Molecular Engineering, Argonne National Laboratory, Lemont, Illinois 60439, United States

E-mail: mgovoni@anl.gov gagalli@uchicago.edu

Abstract

We present a computational protocol, based on density matrix perturbation theory, to obtain non-adiabatic, frequency-dependent electron-phonon self-energies for molecules and solids. Our approach enables the evaluation of electron-phonon interaction using hybrid functionals, for spin-polarized systems, and the computational overhead to include dynamical and non-adiabatic terms in the evaluation of electron-phonon self-energies is negligible. We discuss results for molecules, as well as pristine and defective solids.
1 Introduction

The study of electron-phonon interaction in solids can be traced back to the early days of quantum mechanics,[1] and it has been instrumental in explaining fundamental properties of solids, including conventional superconductivity.[2] However, it was not until recent years that electron-phonon interaction was computed from first-principles,[3–7] leading to non-phenomenological predictions of transport properties of solids[8] and of electron-phonon renormalizations of band structures.[7,9–12] While early studies relied on semi-empirical models[13–15] to study electron-phonon interaction, modern investigations typically employ the frozen phonon (FPH) approach,[7,16] density functional perturbation theory (DFPT),[4,5,10,11,17] or molecular dynamics (MD) simulations,[12,18,19] with electron-electron and electron-ion interactions described at the level of density functional theory (DFT).[20]

In two recent papers,[10,11] we combined first principles calculations of electron–electron and electron–phonon self-energies in molecules and solids, within the framework of density functional perturbation theory (DFPT). We developed an approach that enables the evaluation of electron–phonon coupling at the $G_0W_0$ level of theory for systems with hundreds of atoms, and the inclusion of non-adiabatic and temperature effects at no additional computational cost. We also computed[12] electron-phonon renormalizations of energy gaps by using the path-integral molecular dynamics (PIMD) methods to investigate anharmonic effects in crystalline and amorphous solids. The DFPT, FPH and MD-based methods are addressing different regimes and different problems; the use of DFPT and FPH are appropriate for systems whose atomic constituents all vibrate close to their equilibrium positions, although anharmonic effects have been included in some FPH calculations.[7] The assumption of close to equilibrium vibrations is however not required when applying PIMD, which thus has a wider applicability; for example it can be used to study amorphous materials, and molecules and solids exhibiting prominent anharmonic effects, e.g. molecular crystals[21,22] and several perovskites.[23] However, the calculation of electron-phonon renormalizations using FPH and MD-based methods are carried out within the Allen-Heine-Cardona (AHC)[24,25] formal-
ism, which neglects dynamical and non-adiabatic terms of the electron-phonon self-energies. These effects have been shown to be essential to describe electron-phonon interactions in numerous polar materials, for example SiC. Perturbation-based methods, on the other hand, can accurately compute electron-phonon self-energies within and beyond the AHC formalism, thus including non-adiabatic and/or frequency-dependent effects into the self-energy. Another benefit of DFPT-based method is the ability to explicitly evaluate the electron-phonon coupling matrices which are useful quantities, for example, in the study of mobilities and polaron hopping.

Here we generalize the perturbation-based approach of Ref. 10 and 11 to enable efficient calculations of electron-phonon interaction with hybrid functionals, by using density matrix perturbation theory (DMPT) to compute phonons and electron-phonon coupling matrices. Our implementation takes advantage of the Lanczos algorithm, which enables the calculations of electron-phonon self-energies beyond the AHC approximation, at no extra cost.

DMPT has been used in the literature to compute excitation energies and absorption spectra in molecules and solids in conjunction with time-dependent density functional theory (TDDFT) and to solve the Bethe-Salpeter equation (BSE). In the latter case, DMPT has been applied to obtain the variation of single particle wavefunctions due to the perturbation of an electric field. However, DMPT is a general formalism that can be used to compute the response of a system to perturbations of any form, including perturbations caused by atomic displacements.

In this paper, we first derive a formalism for phonon calculations within DMPT, starting from the quantum Liouville equation in section 2, we then verify our results by comparing them with those of FPH and PIMD calculations in section 3. We then present calculations of electron-phonon interactions in small molecules, pristine and defective diamond using hybrid functionals and we conclude the paper in section 7 with a summary of our findings.


2 Methodology

Using Hartree atomic units \((\hbar = e = m_e = 1)\), we describe the electronic structure of a solid or molecule within Kohn-Sham (KS) density functional theory and we consider the quantum Liouville’s equation to describe perturbations acting on the system:

\[
i \frac{d}{dt} \gamma(t) = [H_{KS}(t), \gamma(t)], \tag{1}
\]

where \([\cdot, \cdot]\) denotes a commutator, \(H_{KS}(t)\) is the Kohn-Sham Hamiltonian

\[
H_{KS} = K + V_H + V_{\text{ext}} + V_{xc}, \tag{2}
\]

with \(K\) the kinetic operator, \(V_H\) the Hartree potential, \(V_{\text{ext}}\) the external potential and \(V_{xc}\) the exchange-correlation potential. The KS Hamiltonian does not depend explicitly on time and depends implicitly on time through the time-dependent density matrix \(\gamma\), that can be written in terms of Kohn-Sham single-particle orbitals \(\psi_{n\sigma}\)

\[
\gamma(\mathbf{r}, \mathbf{r}'; t) = \sum_{\sigma} \sum_{n} N_{\sigma}^{\text{occ}} \psi_{n\sigma}(\mathbf{r}; t) \psi_{n\sigma}^*(\mathbf{r}'; t), \tag{3}
\]

where \(\sigma\) is the spin polarization, \(n\) is the band index and \(N_{\sigma}^{\text{occ}}\) is the number of occupied bands in the spin channel \(\sigma\). Below we present calculations performed by sampling the Brillouin zone with only the \(\Gamma\) point and hence omit labeling eigenstates with \(k\)-points.

Given a time-dependent perturbation \(\partial V_{\text{ext}}(t)\) acting on the Hamiltonian, the first order change of the density matrix \(\partial \gamma(t)\) satisfies the following equation,

\[
i \frac{d}{dt} \partial \gamma(t) = \mathcal{L} \cdot \partial \gamma(t) + [\partial V_{\text{ext}}(t), \gamma_0], \tag{4}
\]

\[
\]

4
where $\mathcal{L}$ is the Liouville super-operator,

$$
\mathcal{L} \cdot \partial \gamma(t) = [H_0^{KS}, \partial \gamma(t)] + [\partial V_{\text{H}}[\partial \gamma(t)], \gamma_0] + [\partial V_{\text{xc}}[\partial \gamma(t)], \gamma_0].
$$

(5)

Here we use the notation $\partial$ to represent a change of potentials ($\partial V$), wavefunctions $\partial \psi$, charge densities $\partial \rho(r)$ and density matrices $\partial \gamma(r, r')$; $\gamma_0$ and $H_0^{KS}$ are the density matrix and the Kohn-Sham Hamiltonian of the unperturbed system, respectively.

Taking the Fourier transform of Eq. (4), we rewrite it in the frequency domain,

$$
(\omega - \mathcal{L}) \cdot \partial \gamma(\omega) = [\partial V_{\text{ext}}(\omega), \gamma_0].
$$

(6)

In phonon calculations, we adopt the Born-Oppenheimer approximation and no retardation effects are included. Hence, we only need to solve Eq. (6) at $\omega = 0$,

$$
\mathcal{L} \cdot \partial \gamma = -[\partial V_{\text{ext}}, \gamma_0].
$$

(7)

The equation above can be cast in the following form:

$$
\begin{bmatrix}
D + K^{1e} - K^{1d} & K^{2e} - K^{2d} \\
-K^{2e} + K^{2d} & -D - K^{1e} + K^{1d}
\end{bmatrix}
\begin{bmatrix}
A \\
B
\end{bmatrix}
= 
\begin{bmatrix}
\{-PC\partial V_{\text{ext}}\psi_{n\sigma} : n = 1, \cdots, N_{\text{occ}}^\sigma; \sigma = \uparrow, \downarrow\} \\
\{PC\partial V_{\text{ext}}\psi_{n\sigma} : n = 1, \cdots, N_{\text{occ}}^\sigma; \sigma = \uparrow, \downarrow\}
\end{bmatrix}
$$

(8)

where $P^c$ is the projection operator onto the virtual bands; $K^{1e}$, $K^{2e}$, $K^{1d}$, $K^{2d}$, defined below in Eq. (12)–(13) and Eq. (15)–(18) are related to the variation of exchange-correlation potential $V_{\text{xc}}$; the elements of the arrays $A = \{a_{n\sigma} : n = 1, \cdots, N_{\text{occ}}^\sigma; \sigma = \uparrow, \downarrow\}$ and $B = \{b_{n\sigma} : n = 1, \cdots, N_{\text{occ}}^\sigma; \sigma = \uparrow, \downarrow\}$ are variations of wavefunctions; the variation of the density matrix in terms of wavefunction variation is:

$$
\partial \gamma = \sum_{\sigma} \sum_{n} N_{\text{occ}}^\sigma 
\begin{bmatrix}
|a_{n\sigma}\rangle \langle \psi_{n\sigma}| + |\psi_{n\sigma}\rangle \langle b_{n\sigma}|
\end{bmatrix}
$$

(9)
In phonon calculations, the external perturbation is static $\partial V_{\text{ext}}(\omega = 0)$, and Eq. (8) can be further simplified since $a_{\nu \sigma} = b_{\nu \sigma} = \partial \psi_{n \sigma}$ for static perturbations and Eq. (8) becomes:

$$[D + \mathcal{K}^{1e} - \mathcal{K}^{1d} + \mathcal{K}^{2e} - \mathcal{K}^{2d}] A = \{ -\mathcal{P}^c \partial V_{\text{ext}} \psi_{n \sigma} : n = 1, \ldots, N_{\text{occ}}^\sigma; \sigma = \uparrow, \downarrow \}.$$  \hspace{1cm} (10)

Eq. (10) is a generalized Sternheimer equation, where the operators on the left hand side are defined below.

$$\mathcal{D} A = \{ \mathcal{P}^c (H_0^{\text{KS}} - \varepsilon_{n \sigma}) | a_{n \sigma} \} : n = 1, \ldots, N_{\text{occ}}^\sigma; \sigma = \uparrow, \downarrow \}.$$ \hspace{1cm} (11)

When using LDA/GGA functionals, the $\mathcal{K}^{1e}$ and $\mathcal{K}^{2e}$ operators are:

$$\mathcal{K}^{1e} A = \left\{ \int \text{d}r' \mathcal{P}^c(r, r') \psi_{n \sigma}(r') \sum_{\sigma'} \sum_{n'}^{N_{\text{occ}}'} \int \text{d}r'' f_{\text{Hxc}}(r', r'') \psi_{n' \sigma'}^*(r'') a_{n' \sigma'}(r'') : n = 1, \ldots, N_{\text{occ}}^\sigma; \sigma = \uparrow, \downarrow \right\},$$ \hspace{1cm} (12)

$$\mathcal{K}^{2e} A = \left\{ \int \text{d}r' \mathcal{P}^c(r, r') \psi_{n \sigma}(r') \sum_{\sigma'} \sum_{n'}^{N_{\text{occ}}'} \int \text{d}r'' f_{\text{Hxc}}(r', r'') a_{n' \sigma'}^*(r'') \psi_{n' \sigma'}(r'') : n = 1, \ldots, N_{\text{occ}}^\sigma; \sigma = \uparrow, \downarrow \right\},$$ \hspace{1cm} (13)

where $f_{\text{Hxc}} = v_c + f_{\text{xc}}$ is the sum of the bare Coulomb potential $v_c$ and the exchange-correlation kernel

$$f_{\text{xc}}(r, r') = \frac{\delta V_{\text{xc}}(r)}{\delta \rho(r')}$$ \hspace{1cm} (14)

with $\rho(r)$ being the electron density.

When using hybrid functionals, the operators are:

$$\mathcal{K}^{1e} A = \left\{ \int \text{d}r' \mathcal{P}^c(r, r') \psi_{n \sigma}(r') \sum_{\sigma'} \sum_{n'}^{N_{\text{occ}}'} \int \text{d}r'' f_{\text{loc}}^{\text{Hxc}}(r', r'') \psi_{n' \sigma'}^*(r'') a_{n' \sigma'}(r'') : n = 1, \ldots, N_{\text{occ}}^\sigma; \sigma = \uparrow, \downarrow \right\},$$ \hspace{1cm} (15)
\[
\mathcal{K}^{2c} A = \left\{ \int d\mathbf{r}' P_c(\mathbf{r}, \mathbf{r}') \psi_{n\sigma}(\mathbf{r}') \sum_{\sigma'} \sum_{n'} N^\sigma_{\text{occ}} \int d\mathbf{r}'' f_{\text{Hxc}}^{\text{loc}}(\mathbf{r}', \mathbf{r}'') a_{n'\sigma'}(\mathbf{r}'') \psi_{n'\sigma'}(\mathbf{r}'') : n = 1, \ldots, N^\sigma_{\text{occ}}; \sigma = \uparrow, \downarrow \right\}, \tag{16}
\]

\[
\mathcal{K}^{1d} A = \left\{ \alpha \int d\mathbf{r}' P_c(\mathbf{r}, \mathbf{r}') \sum_{n'} a_{n'\sigma}(\mathbf{r}') \int d\mathbf{r}'' v_c(\mathbf{r}', \mathbf{r}'') \psi^*_{n'\sigma}(\mathbf{r}'') \psi_{n\sigma}(\mathbf{r}'') : n = 1, \ldots, N^\sigma_{\text{occ}}; \sigma = \uparrow, \downarrow \right\}, \tag{17}
\]

\[
\mathcal{K}^{2d} A = \left\{ \alpha \int d\mathbf{r}' P_c(\mathbf{r}, \mathbf{r}') \sum_{n'} \psi_{n'\sigma}(\mathbf{r}') \int d\mathbf{r}'' v_c(\mathbf{r}', \mathbf{r}'') a_{n'\sigma}(\mathbf{r}'') \psi_{n\sigma}(\mathbf{r}'') : n = 1, \ldots, N^\sigma_{\text{occ}}; \sigma = \uparrow, \downarrow \right\}, \tag{18}
\]

where \( f^{\text{loc}}_{\text{Hxc}} = v_c + f^{\text{loc}}_{\text{xc}} \) is the sum of the bare Coulomb potential and the local part of the exchange-correlation kernel

\[
f^{\text{loc}}_{\text{xc}}(\mathbf{r}, \mathbf{r}') = \frac{\delta V^{\text{loc}}_{\text{xc}}(\mathbf{r})}{\delta \rho(\mathbf{r}')}, \tag{19}
\]

and the parameter \( \alpha \) is the fraction of the Hartree-Fock exchange included in the definition of the hybrid functional. Note that the \( \mathcal{K}^{1d} \) and the \( \mathcal{K}^{2d} \) operators are zero for LDA/GGA functionals.

Once we have the solutions \( a_{n\sigma} \) of the Liouville equation (Eq. (8) or Eq. (10)), i.e., the change of wavefunction \( \partial \psi_{n\sigma} \), we can compute the change of the density matrix with Eq. (9); the change of density is then given by:

\[
\partial \rho(\mathbf{r}) = \partial \gamma(\mathbf{r}, \mathbf{r}) = \sum_{\sigma} \sum_{n} N^\sigma_{\text{occ}} \left[ \partial \psi^*_{n\sigma}(\mathbf{r}) \psi_{n\sigma}(\mathbf{r}) + \psi^*_{n\sigma}(\mathbf{r}) \partial \psi_{n\sigma}(\mathbf{r}) \right] \tag{20}
\]

and force constants are obtained as follows:

\[
C_{I\alpha,I\beta} \propto \sum_{\sigma} \sum_{n} \langle \partial_{I\alpha} \psi_{n\sigma} | \partial_{I\beta} V_{\text{ext}} | \psi_{n\sigma} \rangle. \tag{21}
\]
By diagonalizing the dynamical matrix,
\[ \sum_{J\beta} \frac{1}{\sqrt{M_I M_J}} C_{I\alpha, J\beta \xi_{J\beta, \nu}} = \omega_{\nu}^2 \xi_{I\alpha, \nu}, \]  
(22)

where \( M_I, M_J \) are atomic masses, we obtain the frequency \( \omega_{\nu} \) of mode \( \nu \) and its polarization \( \xi_{I\alpha, \nu} \).

To compute the electron-phonon coupling matrices in the Cartesian basis:
\[ g_{m\sigma I\alpha}^\sigma = \langle \psi_{m\sigma} | \partial_{I\alpha} V_{\text{scf}} | \psi_{n\sigma} \rangle \]  
(23)
or in the phonon mode basis:
\[ g_{m\nu}^\sigma = \sum_{I\alpha} \xi_{I\alpha, \nu} \sqrt{M_I} g_{m\sigma I\alpha} \]  
(24)

where \( \xi_{I\alpha, \nu} \) is the \( \nu \)-th vibrational mode, we need to evaluate the change of the self-consistent (scf) potential \( \partial V_{\text{scf}} \). The scf potential is given by the sum of the Hartree potential \( V_H \), the local part of the exchange-correlation potential \( V_{\text{xc}}^{\text{loc}} \) and the non-local Hatree-Fock exchange \( V_{\text{xc}}^{\text{nl}} \). Thus, the change of the scf potential \( \partial V_{\text{scf}} | \psi_{n\sigma} \rangle \) is the sum of the following three terms:
\[ \partial V_H(r) | \psi_{n\sigma}(r) \rangle = \psi_{n\sigma}(r) \int \text{d}r' v_c(r, r') \partial \rho(r'), \]  
(25)
\[ \partial V_{\text{xc}}^{\text{loc}}(r) | \psi_{n\sigma}(r) \rangle = \psi_{n\sigma}(r) \int \text{d}r' f_{\text{Hxc}}^{\text{loc}}(r, r') \partial \rho(r'), \]  
(26)
and
\[ \partial V_{\text{xc}}^{\text{nl}} | \psi_{n\sigma} \rangle = -\alpha \sum_{N_{\text{xc}}} \int \text{d}r' [ \partial \psi^\dagger_{n'\sigma}(r') \psi_{n'\sigma}(r) + \psi^\dagger_{n'\sigma}(r') \partial \psi_{n'\sigma}(r) ] v_c(r, r') \psi_{n\sigma}(r'). \]  
(27)

The Fan-Migdal and Debye-Waller self-energies can then be computed as:
\[ \langle \psi_{n\sigma} | \Sigma_{\text{FM}}(\omega, T) | \psi_{n\sigma} \rangle = \sum_{mn\nu} |g_{mn\nu}^\sigma|^2 \left[ \frac{b_{\nu}(T) + f_{m\sigma}(T)}{\omega - \varepsilon_{m\sigma} + \omega_{\nu} - i0^+} + \frac{b_{\nu}(T) + 1 - f_{m\sigma}(T)}{\omega - \varepsilon_{m\sigma} - \omega_{\nu} - i0^+} \right] \]  
(28)
\[ \langle \psi_{n\sigma}|\Sigma^{\text{DW}}(T)|\psi_{n\sigma}\rangle = -\sum_{m\nu} \sum_{I\alpha,J\beta} \left[ \frac{2b_{\nu}(T) + 1}{\varepsilon_{n\sigma} - \varepsilon_{m\sigma}} \left( \frac{\xi_{I\alpha,\nu}\xi_{J\beta,\nu}}{M_I} + \frac{\xi_{I\alpha,\nu}\xi_{J\beta,\nu}}{M_J} \right) \right] g_{mnI\alpha}^\sigma g_{mnJ\beta}^\sigma, \] (29)

where \( b_{\nu} \) is the occupation number of the frequency \( \omega_{\nu} \) obeying the Bose-Einstein distribution and \( f_{m\sigma} \) is the occupation number of the Kohn-Sham eigenvalues \( \varepsilon_{m\sigma} \) obeying the Fermi-Dirac distribution. The Debye-Waller self-energy is derived within the rigid-ion approximation (RIA), which approximates second-order electron-phonon coupling matrices with first-order ones.

Using the frequency-dependent Fan-Migdal self-energy, the renormalized energy levels can be evaluated self-consistently,

\[ \omega - \varepsilon_{n\sigma} = \langle \psi_{n\sigma}|\Sigma^{\text{FM}}(\omega,T) + \Sigma^{\text{DW}}(T)|\psi_{n\sigma}\rangle \] (30)

with initial guess \( \omega_0 = \varepsilon_{n\sigma} \), and using the Lanczos algorithm to evaluate the frequency-dependent Fan-Migdal self-energy (for a detailed derivation, see Ref. 10 and Ref. 11).

We refer to the FM self-energy in Eq. 28 as the non-adiabatic fully frequency-dependent (NA-FF) self-energy. If the frequency-dependence is considered within the adiabatic approximation, the self-energy is

\[ \langle \psi_{n\sigma}|\Sigma_{\text{A-FF}}^{\text{FM}}(\omega,T)|\psi_{n\sigma}\rangle \simeq \sum_{m\nu} |g_{mnI\alpha}^\sigma|^2 \left( \frac{2b_{\nu}(T) + 1}{\omega - \varepsilon_{m\sigma}} \right). \] (31)

We refer to Eq. 31 as the adiabatic fully frequency-dependent (A-FF) self-energy.

In our formulation the evaluation of self-energies can be carried out simultaneously at multiple frequencies using the Lanczos algorithm; however, we introduce below approximations leading to frequency independent self-energies for comparison with results present in the literature, obtained e.g., with the Allen-Heine-Cardona (AHC) formalism. In particular, we evaluate the FM self-energy by applying the so-called On-the-Mass-Shell (OMS) approximation, i.e., by setting \( \omega = \varepsilon_{n\sigma} \) in the expressions of the A-FF and NA-FF self-energies. In the former case we obtain the adiabatic AHC (A-AHC) approximation and
in the latter case the non-adiabatic AHC (NA-AHC) approximation:

\[
\langle \psi_{n\sigma} | \Sigma_{A-AHC}^{FM}(T) | \psi_{n\sigma} \rangle \simeq \sum_{m\nu} |g_{mn\nu}^\sigma|^2 \frac{2b_\nu(T) + 1}{\varepsilon_{n\sigma} - \varepsilon_{m\sigma}} (32)
\]

\[
\langle \psi_{n\sigma} | \Sigma_{NA-AHC}^{FM}(T) | \psi_{n\sigma} \rangle = \sum_{m\nu} |g_{mn\nu}^\sigma|^2 \left[ \frac{b_\nu(T) + f_{m\sigma}(T)}{\varepsilon_{n\sigma} - \varepsilon_{m\sigma} + \omega_\nu - i0^+} + \frac{b_\nu + 1 - f_{m\sigma}}{\varepsilon_{n\sigma} - \varepsilon_{m\sigma} - \omega_\nu - i0^+} \right]. (33)
\]

We summarize the various levels of approximations applied to evaluate the FM self-energy in Table 1; the corresponding DW self-energies are the same for all levels of approximation. Thus, we also use the acronyms A-AHC, NA-AHC, A-FF and NA-FF to denote the level of theory adopted for the total self-energy (FM + DW) and for the electron-phonon renormalization of fundamental gaps.

Table 1: A list of theoretical approximations used in this paper to compute the Fan-Migdal self-energy, where we specify whether the on-the-mass-shell (OMS) and the adiabatic approximation are adopted (✓) or not adopted (×).

| Level of theory | OMS | Adiabatic | Equation |
|-----------------|-----|-----------|----------|
| (A-)AHC         | ✓   | ✓         | 32       |
| NA-AHC          | ✓   | ×         | 33       |
| A-FF            | ×   | ✓         | 31       |
| NA-FF           | ×   | ×         | 28       |

a In the main text, we use AHC and A-AHC interchangeably.

3 Verification

To verify the implementation of the method described above in the WEST package, we first computed the phonon frequencies of selected solids (diamond, silicon and silicon carbide) and the vibrational modes of selected molecules (\(H_2, N_2, H_2O, CO_2\)), and compared our results with those of the frozen phonon approach. In Table 2 and Table 3, we summarize our results obtained at the PBE0 level of theory and obtained by solving either the Liouville equation
or by using the frozen phonon approach. The lattice constants used for diamond, silicon and silicon carbide are 3.635, 5.464 and 4.372 Å, respectively, and the cell used for molecules is a cube of edge 10.583 Å. For verification purposes, we only computed the phonon modes at the Γ point in the Brillouin zone of the solids. We used an energy cutoff of 60 Ry for the solids and 50 Ry for the molecules, and the SG15 ONCV pseudopotentials for all solids and molecules.

Table 2 shows that the absolute difference of the phonon frequencies computed with the FPH approach and the method implemented here are small for silicon and silicon carbide, 0.19 and 0.07 cm\(^{-1}\), respectively. The corresponding difference for diamond is larger, but still acceptable being below 5 cm\(^{-1}\). In Table 3 we compare the vibrational frequencies of H\(_2\), N\(_2\), H\(_2\)O and CO\(_2\) molecules computed by solving the Liouville equation and applying the frozen-phonon approach. We found again that the differences are small for N\(_2\) and CO\(_2\) (below 1 cm\(^{-1}\)), albeit slightly larger for H\(_2\) and H\(_2\)O. The largest difference is found in the case of H\(_2\) (17.30 cm\(^{-1}\)), and this is most likely due to the numerical inaccuracy of the frozen-phonon approach.

Table 2: A comparison of selected phonon frequencies [cm\(^{-1}\)] in diamond, silicon and silicon carbide computed in a primitive cell with the PBE0 functional by solving the Liouville’s equation or by using the frozen-phonon approach.

| Solid             | Liouville | Frozen-phonon | Absolute difference |
|-------------------|-----------|--------------|---------------------|
| diamond           | 2136.21   | 2131.48      | 4.73                |
| silicon           | 737.47    | 737.28       | 0.19                |
| silicon carbide   | 612.77    | 612.70       | 0.07                |

To verify our calculations of electron-phonon interactions, we carried out a detailed study of the renormalization of the HOMO-LUMO gaps (\(E_g\)) of the CO\(_2\), Si\(_2\)H\(_6\), HCN, HF and N\(_2\) molecules, with the results for CO\(_2\) summarized in Table 4 and the rest in Table 5.

Table 4 summarizes the renormalizations to the \(E_g\) of the CO\(_2\) molecule obtained within the A-AHC formalism, and using DFPT, FPH and path-integral molecular dynamics (PIMD) at the LDA, PBE, PBE0 and B3LYP levels of theory, respectively. With the LDA
Table 3: A comparison of the vibrational modes [cm$^{-1}$] of selected molecules obtained with the PBE0 functional and computed by solving the Liouville’s equation or by using the frozen-phonon approach. The symmetry of the mode is given in the second column.

| Molecule | Symmetry | Liouville | Frozen-phonon | Absolute difference |
|----------|----------|-----------|---------------|---------------------|
| H$_2$    | $a_1$    | 4421.48   | 4438.78       | 17.30               |
| N$_2$    | $a_1$    | 2480.36   | 2480.36       | 0.00                |
| H$_2$O   | $a_1$    | 1652.79   | 1658.76       | 5.97                |
| H$_2$O   | $b_2$    | 3921.28   | 3936.57       | 15.29               |
| H$_2$O   | $a_1$    | 4033.68   | 4048.58       | 11.90               |
| CO$_2$   | $e_{1u}$ | 698.15    | 698.12        | 0.03                |
| CO$_2$   | $a_{1g}$ | 1375.10   | 1375.18       | 0.08                |
| CO$_2$   | $a_{1u}$ | 2419.08   | 2419.23       | 0.15                |

and PBE/GGA functionals, the solution of the Liouville equation yields the same results as the method proposed in Ref. [10] and Ref. [11] as expected. When solving the Liouville equation with the DFPT method, the rigid-ion approximation is adopted, however the latter approximation is not used in the frozen-phonon approach, leading to a slight difference between the frozen-phonon and Liouville results. In addition, we carried out calculations with the hybrid functionals, PBE0 and B3LYP, and compared our results with those of the frozen-phonon and PIMD approaches. The PIMD approach circumvents the rigid-ion approximation and also includes ionic anharmonic effects. Since the rigid-ion approximation is adopted and anharmonicity is not included in the Liouville approach, differences on the order of $\sim 30$ meV, relative to PIMD are considered as acceptable. We note that the computed renormalizations of the gap of CO$_2$ reported in the literature, $-680.7$ and $-716.2$ meV with LDA and PBE+TS functionals, respectively, are significantly different from those obtained here. We also note that Ref. [55] reports a result at the B3LYP level of theory, $-4091.6$ meV, which is one order of magnitude larger than the corresponding LDA and PBE+TS results, hence calling into question the numerical accuracy of the data. Such significant differences between our and the results of Ref. [55] probably stems from the different choices of basis functions, localized basis functions in Ref. [55] and plane-waves in this work.
In addition to CO$_2$, we also computed the energy gap renormalizations of Si$_2$H$_6$, HCN, HF and N$_2$ molecules with the B3LYP functional; these are shown in Table 5. For Si$_2$H$_6$ and HCN, the results computed with the Liouville’s equation and the FPH approach agree well, with small differences of 22 and 5 meV, respectively. The renormalization of HF is about $-20$ meV with both the Liouville and FPH approaches, consistent with the result $-29.9$ meV reported in literature. The Liouville and FPH methods both predict the renormalization of N$_2$ to be close to zero, in agreement with Ref. 55.

In summary, we have verified our implementation of phonon and electron-phonon interaction by comparing results computed with the Liouville’s equation and those obtained with DFPT, FPH and PIMD methods. At the LDA/PBE level of theories, we obtain exactly the same results as with DFPT, as expected; at the hybrid functional level of theory, the results obtained with the Liouville’s equation are comparable with those of the FPH and PIMD methods, with reasonable differences compatible with the different approximations employed in the three different approaches.

4 Electron-phonon renormalization of energy gaps in small molecules

Having verified our implementation, we carried out a study of the renormalization of the HOMO-LUMO gap of molecules in the G2/97 test set with LDA, PBE, PBE0 and B3LYP functionals. The results are summarized in Table 6 and Table 7, and are illustrated in Figure 1.

Table 6 summarizes the renormalizations computed with the A-AHC formalism. For most of the molecules, using hybrid functionals does not significantly change the gap renormalization relative to LDA or PBE results. For example, the energy gap renormalizations of the H$_2$ molecule computed with LDA, PBE, PBE0 and B3LYP functionals are 58 meV, 61 meV, 63 meV and 63 meV, respectively. However, hybrid functionals do reduce the magnitude of
Table 4: Electron-phonon renormalization energies [meV] of HOMO, LUMO energy levels and the HOMO-LUMO gap in the CO$_2$ molecule, computed by solving the Liouville’s equation, using density functional perturbation theory (DFPT), the frozen-phonon (FPH) approach and the path-integral molecular dynamics (PIMD) method. We compare results obtained with different functionals: LDA, PBE, PBE0 and the B3LYP functionals, and include results obtained in Ref. 55.

| Method  | Functional | HOMO Renorm. | LUMO Renorm. | Gap Renorm. |
|---------|------------|---------------|---------------|--------------|
| Liouville | LDA | 64 | -453 | -517 |
| DFPT | LDA | 64 | -453 | -517 |
| Liouville | PBE | 65 | -350 | -415 |
| DFPT | PBE | 65 | -350 | -415 |
| FPH | PBE | 53 | -325 | -378 |
| Liouville | PBE0 | 68 | -69 | -137 |
| FPH | PBE0 | 55 | -77 | -132 |
| PIMD | PBE0 | 59 | -103 | -162 |
| Liouville | B3LYP | 67 | -107 | -174 |
| FPH | B3LYP | 54 | -89 | -143 |
| PIMD | B3LYP | 58 | -112 | -170 |
| Ref. [55] | LDA | — | — | -680.7 |
| PBE+TS | — | — | -716.2 |
| B3LYP | — | — | -4091.6 |

Table 5: Electron-phonon renormalization energies [meV] of energy gap in Si$_2$H$_6$, HCN, HF and N$_2$ molecules computed by solving the Liouville’s equation and using the frozen phonon (FPH) approach at the B3LYP level of theory.

| Molecule | Liouville | FPH | Ref. [55] |
|----------|-----------|-----|-----------|
| Si$_2$H$_6$ | -117 | -139 | -1872.3 |
| HCN | -19 | -14 | -171.4 |
| HF | -18 | -25 | -29.9 |
| N$_2$ | 8 | -6 | 8.7 |
gap renormalization in several systems, and CO$_2$ and CH$_3$Cl are representative examples. In CO$_2$ the renormalization is reduced from $-415$ meV (PBE) to $-137$ meV (PBE0) level of theory; in CH$_3$Cl, it is reduced from $-149$ meV (PBE) to $-59$ meV (PBE0).

We report in Table 7 our results within the non-adiabatic AHC (NA-AHC) framework. The removal of the adiabatic approximation significantly influences the computed magnitude of the gap renormalization in most of the molecules, with some exceptions, e.g. CO$_2$. For example, the H$_2$ gap renormalization computed using PBE0 varies from 63 meV (AHC) to $-377$ meV (NA-AHC). The most significant differences are found for the F$_2$ and H$_2$O$_2$ molecules, where the gap renormalizations computed at the PBE0 level of theory are 25 and $-72$ meV, respectively, within the AHC approach and $-2914$ and $-891$ meV, when using the non-adiabatic AHC method.

![Figure 1: Computed zero-point renormalization energies of the HOMO-LUMO gaps of small molecules using the AHC (upper panel) and NA-AHC (lower panel) approximations (see Table 1. for the definition of the approximations). We used different functionals specified in the inset.](image)

We emphasize that neither the AHC nor the non-adiabtic AHC formalism correctly de-
Table 6: HOMO-LUMO energy gaps of small molecules and their zero-point renormalization energy (ZPR) computed within the adiabatic Allen-Heine-Cardona (A-AHC) approximation. All gaps and ZPRs are in eV. We compare results obtained with different energy functionals (LDA, PBE, PBE0 and B3LYP) and we also report ZPRs from Ref. [55] and, in few cases, Ref. [45]

| Molecule | LDA | PBE | PBE0 | B3LYP |
|----------|-----|-----|------|-------|
|          | gap | ZPR | Ref. | gap | ZPR | gap | ZPR | Ref. | gap | ZPR | Ref. |
| H\textsubscript{2} | 9.998 | 0.058 | -0.002 | 10.164 | 0.061 | 11.890 | 0.063 | 11.648 | 0.063 | 0.0036 |
| LiF      | 5.108 | 0.006 | 0.0331 | 4.723 | 0.006 | 7.014 | 0.007 | 6.601 | 0.007 | 0.0040 |
| N\textsubscript{2} | 8.221 | 0.013 | 0.0118 | 8.319 | 0.013 | 11.707 | 0.007 | 11.179 | 0.008 | 0.0087 |
| CO       | 6.956 | 0.005 | 0.0130a | 7.074 | 0.004 | 10.055 | -0.003 | 9.575 | -0.002 | 0.0024 |
| ClF      | 3.194 | 0.004 | 0.0065a | 3.167 | 0.005 | 6.250 | -0.002 | 5.629 | -0.001 | 0.0025 |
| CS       | 3.954 | -0.004 | 0.0041 | 4.042 | -0.004 | 6.562 | -0.006 | 6.199 | -0.006 | -0.0058 |
| HF       | 8.681 | -0.032 | 0.007a | 8.598 | -0.030 | 11.302 | -0.011 | 10.809 | -0.018 | -0.0299 |
| NaCl     | 3.524 | 0.002 | 0.0001 | 3.225 | 0.002 | 5.069 | 0.002 | 4.577 | 0.002 | 0.0004 |
| SiO      | 4.524 | 0.001 | 0.0001 | 4.549 | 0.001 | 6.764 | -0.002 | 6.368 | -0.002 | -0.0032 |
| Cl\textsubscript{2} | 2.899 | 0.006 | 0.0063 | 2.894 | 0.006 | 5.503 | 0.002 | 4.887 | 0.003 | 0.0060 |
| F\textsubscript{2} | 3.495 | 0.030 | 0.0369 | 3.370 | 0.029 | 7.480 | 0.025 | 6.917 | 0.025 | 0.0329 |
| Li\textsubscript{2} | 1.532 | 0.001 | 0.0006 | 1.524 | 0.001 | 2.582 | 0.001 | 2.343 | 0.001 | 0.0007 |
| LiH      | 2.985 | 0.002 | 0.0002 | 2.873 | 0.003 | 4.424 | 0.001 | 4.117 | 0.002 | -0.0061 |
| Na\textsubscript{2} | 1.564 | 0.001 | 0.0002 | 1.521 | 0.001 | 2.495 | 0.000 | 2.264 | 0.001 | 0.0000 |
| P\textsubscript{2} | 3.649 | 0.005 | 0.0021 | 3.644 | 0.005 | 5.537 | 0.005 | 5.107 | 0.005 | 0.0037 |
| CO\textsubscript{2} | 8.075 | -0.517 | -0.6807 | 8.033 | -0.415 | 10.159 | -0.137 | 9.708 | -0.174 | -0.4916 |
| HCN      | 7.878 | -0.185 | -0.1412 | 7.930 | -0.190 | 10.186 | -0.020 | 9.806 | -0.019 | -0.1714 |
| H\textsubscript{2}O | 6.272 | -0.042 | -0.0806 | 6.208 | -0.036 | 8.511 | -0.013 | 8.084 | -0.020 | -0.0524 |
| SH\textsubscript{2} | 5.212 | -0.189 | -0.0360 | 5.238 | -0.160 | 6.942 | -0.042 | 6.593 | -0.059 | -0.2117 |
| SO\textsubscript{2} | 3.457 | -0.019 | -0.0178 | 3.414 | -0.021 | 6.087 | -0.016 | 5.596 | -0.018 | -0.0186 |
| H\textsubscript{2}CO | 3.470 | -0.091 | -0.0876 | 3.589 | -0.092 | 6.451 | -0.114 | 5.993 | -0.111 | -0.1005 |
| H\textsubscript{2}O\textsubscript{2} | 5.028 | -0.093 | -0.1290 | 4.887 | -0.071 | 7.780 | -0.072 | 7.505 | -0.110 | -0.2254 |
| NH\textsubscript{3} | 5.395 | -0.053 | -0.0611 | 5.304 | -0.048 | 7.205 | -0.035 | 6.825 | -0.038 | -0.0333 |
| PH\textsubscript{3} | 5.999 | -0.146 | -0.0592 | 5.946 | -0.110 | 7.388 | -0.039 | 7.056 | -0.047 | -0.2017 |
| C\textsubscript{2}H\textsubscript{2} | 6.703 | -0.179 | -0.1901 | 6.712 | -0.029 | 8.181 | -0.016 | 7.835 | -0.014 | -0.2327 |
| CH\textsubscript{3}Cl | 6.327 | -0.158 | -0.1441 | 6.210 | -0.149 | 8.042 | -0.059 | 7.691 | -0.068 | -0.1141 |
| CH\textsubscript{4} | 8.799 | -0.084 | -0.1147 | 8.820 | -0.081 | 10.647 | -0.091 | 10.320 | -0.090 | -0.0947 |
| SiH\textsubscript{4} | 7.727 | -0.141 | -0.6149 | 7.772 | -0.115 | 9.440 | -0.083 | 9.187 | -0.086 | -0.2027 |
| N\textsubscript{2}H\textsubscript{4} | 4.892 | -0.386 | -0.1169 | 4.866 | -0.383 | 6.736 | -0.375 | 6.426 | -0.359 | -0.0793 |
| C\textsubscript{2}H\textsubscript{4} | 5.654 | -0.129 | -0.1358 | 5.673 | -0.123 | 7.592 | -0.059 | 7.224 | -0.053 | -0.1194 |
| Si\textsubscript{2}H\textsubscript{6} | 6.364 | -0.305 | -0.5880 | 6.386 | -0.238 | 7.874 | -0.117 | 7.609 | -0.117 | -1.8723 |

\* Ref. [45]
Table 7: HOMO-LUMO gaps of small molecules and their zero-point renormalization energies (ZPR) computed within the non-adiabatic Allen-Heine-Cardona (NA-AHC) approximation. All gaps and ZPRs are in eV. We compare results obtained with different energy functionals (LDA, PBE, PBE0, B3LYP).

| Molecule | LDA | | PBE | | PBE0 | | B3LYP | |
|----------|-----|-----|-----|-----|-----|-----|-----|
|          | gap | ZPR | gap | ZPR | gap | ZPR | gap | ZPR |
| H₂       | 9.998 | -0.260 | 10.164 | -0.263 | 11.890 | -0.377 | 11.648 | -0.366 |
| LiF      | 5.108 | -0.123 | 4.723 | -0.122 | 7.014 | -0.134 | 6.601 | -0.134 |
| N₂       | 8.221 | -0.418 | 8.319 | -0.432 | 11.707 | -0.418 | 11.179 | -0.428 |
| CO       | 6.956 | -0.361 | 7.074 | -0.373 | 10.055 | -0.338 | 9.575 | -0.346 |
| ClF      | 3.194 | -0.959 | 3.167 | -0.985 | 6.250 | -1.011 | 5.629 | -1.000 |
| CS       | 3.954 | -0.151 | 4.042 | -0.156 | 6.562 | -0.155 | 6.199 | -0.154 |
| HF       | 8.681 | -0.225 | 8.598 | -0.194 | 11.302 | -0.083 | 10.809 | -0.111 |
| NaCl     | 3.524 | -0.021 | 3.225 | -0.022 | 5.069 | -0.022 | 4.577 | -0.022 |
| SiO      | 4.524 | -0.052 | 4.549 | -0.054 | 6.764 | -0.056 | 6.368 | -0.055 |
| Cl₂      | 2.899 | -0.557 | 2.894 | -0.560 | 5.503 | -0.622 | 4.887 | -0.589 |
| F₂       | 3.495 | -2.405 | 3.370 | -2.317 | 7.840 | -2.914 | 6.917 | -2.600 |
| HCl      | 6.768 | -0.052 | 6.784 | -0.054 | 8.511 | -0.050 | 8.084 | -0.061 |
| Li₂      | 1.532 | -0.007 | 1.524 | -0.008 | 2.582 | -0.010 | 2.343 | -0.010 |
| LiH      | 2.985 | -0.049 | 2.873 | -0.045 | 4.424 | -0.055 | 4.117 | -0.058 |
| Na₂      | 1.564 | -0.002 | 1.521 | -0.002 | 2.495 | -0.002 | 2.264 | -0.002 |
| P₂       | 3.649 | -0.077 | 3.644 | -0.079 | 5.537 | -0.100 | 5.107 | -0.096 |
| CO₂      | 8.075 | -0.495 | 8.033 | -0.398 | 10.159 | -0.136 | 9.708 | -0.174 |
| HCN      | 7.878 | -0.543 | 7.930 | -0.541 | 10.186 | -0.147 | 9.806 | -0.138 |
| H₂O      | 6.272 | -0.114 | 6.208 | -0.095 | 8.511 | -0.050 | 8.084 | -0.061 |
| SH₂      | 5.212 | -0.203 | 5.238 | -0.166 | 6.942 | -0.050 | 6.593 | -0.069 |
| SO₂      | 3.457 | -0.231 | 3.414 | -0.234 | 6.087 | -0.281 | 5.596 | -0.274 |
| H₂CO     | 3.470 | -0.364 | 3.589 | -0.376 | 6.451 | -0.386 | 5.993 | -0.382 |
| H₂O₂     | 5.028 | -2.549 | 4.887 | -2.582 | 7.780 | -0.891 | 7.505 | -0.799 |
| NH₃      | 5.395 | -0.590 | 5.304 | -0.566 | 7.205 | -0.578 | 6.825 | -0.562 |
| PH₃      | 5.999 | -0.516 | 5.946 | -0.493 | 7.388 | -0.453 | 7.056 | -0.450 |
| C₂H₂     | 6.703 | -0.420 | 6.712 | -0.074 | 8.181 | -0.080 | 7.835 | -0.073 |
| CH₃Cl    | 6.323 | -0.351 | 6.210 | -0.307 | 8.042 | -0.112 | 7.691 | -0.116 |
| CH₄      | 8.799 | -1.950 | 8.820 | -1.961 | 10.647 | -2.245 | 10.320 | -2.210 |
| SiH₄     | 7.727 | -0.931 | 7.772 | -0.916 | 9.440 | -1.019 | 9.187 | -1.007 |
| N₂H₄     | 4.892 | -1.082 | 4.866 | -1.038 | 6.736 | -1.129 | 6.426 | -1.050 |
| C₂H₄     | 5.654 | -0.408 | 5.673 | -0.411 | 7.592 | -0.184 | 7.224 | -0.173 |
| Si₂H₆    | 6.364 | -0.607 | 6.386 | -0.551 | 7.874 | -0.506 | 7.609 | -0.507 |
scribes the self-energies in the full energy range, and thus we suggest that the frequency-dependent self-energies should always be computed.

5 Electron-phonon renormalization of the energy gap of diamond

We computed the electron-phonon renormalization of the energy gap in diamond within the AHC formalism, and by computing the NA-FF self-energies self-consistently (see Table 1 and Eq. (30)). The calculations for diamond were carried out in a $3 \times 3 \times 3$ supercell.

In Figure 2, we present the temperature-dependent indirect gap renormalization computed with the PBE, PBE0 and dielectric dependent hybrid (DDH) functionals, where the fraction of exact exchange (0.18) in DDH is chosen to be the inverse of the dielectric constant of diamond (5.61). Within the same level of approximation, e.g., the AHC formalism (circles in the plot), the PBE, PBE0 and DDH results are almost the same for temperatures lower than 400 K, but their difference increases at higher temperatures. With the same functional, e.g., the PBE0 functional (orange lines in the plot), the results obtained with the fully frequency-dependent non-adiabatic self-energies are lower than those obtained with the AHC formalism. In general, the use of the hybrid functional does not significantly modify the trend of the ZPRs computed at the PBE level, as a function of temperature.

In Figure 2, we also report the renormalization of the indirect gap of diamond obtained with the frozen phonon approach and the PBE0 functional. The results obtained with the FPH (purple line) approach and the Liouville equation (orange lines in the plot) are essentially the same below 300 K, but they differ as T is increased. The difference between the AHC/NA-FF and FPH approaches is always smaller than 10 meV at all temperatures, and it is reasonable considering that the FPH approach does not adopt the rigid-ion approximation, which is instead used within the AHC and NA-FF approaches.

A comparison of the computed and measured renormalized energy gap of diamond is
Figure 2: The electron-phonon renormalization energy of the indirect band gap of diamond computed by solving the Liouville equation and with different approximations to the self-energy, as defined in Table 1. The results obtained with the frozen phonon (FPH) approach and the PBE0 functional are also reported for comparison. The renormalization energy at zero temperature has been shifted to zero.

Figure 3: The electron-phonon renormalized indirect energy gap in diamond computed with the PBE and PBE0 functionals compared to experimental measurements. We show calculations performed with different approximations, as defined in Table 1.
Table 8: The temperature-dependent zero-point renormalization energy (ZPR) and renormalized indirect energy gap (Gap+ZPR) computed with the PBE, PBE0 and DDH functionals, using different levels of approximations, as defined in Table 1. The energy gaps computed at the PBE, PBE0 and DDH level of theory, without electron-phonon interaction, are 4.144, 6.189 and 5.597 eV respectively. All energies are reported in eV.

| Functional | Temperature [K] | Method |
|------------|-----------------|--------|
| ZPR        | 0               | 100    | 200  | 300  | 400  | 500  | 600  |
| PBE        | AHC             | -0.281 | -0.281 | -0.282 | -0.284 | -0.291 | -0.303 | -0.320 |
|            | NA-FF           | -0.438 | -0.438 | -0.438 | -0.441 | -0.448 | -0.463 | -0.483 |
| PBE0       | AHC             | -0.290 | -0.290 | -0.290 | -0.291 | -0.297 | -0.308 | -0.323 |
|            | NA-FF           | -0.454 | -0.454 | -0.454 | -0.456 | -0.463 | -0.476 | -0.495 |
| DDH        | AHC             | -0.289 | -0.289 | -0.289 | -0.291 | -0.297 | -0.308 | -0.324 |
|            | NA-FF           | -0.450 | -0.450 | -0.450 | -0.451 | -0.458 | -0.472 | -0.492 |
| Gap+ZPR    | PBE             | 3.862  | 3.862  | 3.862  | 3.860  | 3.853  | 3.840  | 3.824  |
|            | NA-FF           | 3.705  | 3.705  | 3.705  | 3.703  | 3.695  | 3.681  | 3.661  |
|            | PBE0            | 5.899  | 5.899  | 5.899  | 5.898  | 5.892  | 5.881  | 5.866  |
|            | NA-FF           | 5.735  | 5.735  | 5.735  | 5.733  | 5.726  | 5.713  | 5.694  |
|            | DDH             | 5.308  | 5.308  | 5.308  | 5.306  | 5.300  | 5.289  | 5.274  |
|            | NA-FF           | 5.148  | 5.148  | 5.148  | 5.146  | 5.139  | 5.125  | 5.106  |
given in Figure 3 and Table 8. Although the PBE0 and DDH hybrid functionals yield a
similar trend as PBE for the electron-phonon renormalization as a function of temperature,
the renormalized gap are noticeably improved compared to experiments when using hybrid
functionals. The indirect energy gap of diamond computed with PBE, PBE0 and DDH
without electron-phonon renormalization are 4.144, 6.189, and 5.597 eV, respectively, and
the experimental indirect gap measured at approximately 100 K is 5.45 eV.\textsuperscript{60} By including
electron-phonon renormalization, we can see that the results computed at the PBE0 level of
theory agree relatively well with the experimental measurements (see Figure 3 and Table 8).
The renormalized indirect gap computed with the PBE0 functional at 100 K is 5.899 eV
when the AHC formalism is used, and it is 5.735 eV when the NA-FF self-energies are
used. The renormalized indirect gaps computed with the DDH functional at 100 K are 5.308
(AHC) and 5.148 eV (NA-FF). As expected, the DDH results are closer to experimental
measurements compared with those of the PBE0 functional, since the fraction of exact
exchange is chosen according to the system specific dielectric constant. Overall we find that
computing electron-phonon interactions at the hybrid level of theory is a promising protocol
to obtain quantitative results, comparable to experiments.

6 Application to spin defects in diamond

Spin defects have been extensively studied due to their potential applications in quantum
technologies.\textsuperscript{61–64} To accurately predict the electronic structures of spin defects, we computed
their electronic properties using electron-phonon renormalizations and we considered a single
Boron defect and the NV\textsuperscript{−} center shown in Figure 4. The calculations were carried out in a
2 × 2 × 2 cubic cell (63 atoms for NV\textsuperscript{−} center and 64 atoms for single Boron defect).

In Table 9 and Table 10 we report the electronic energy levels and zero-point renor-
malization for both defects obtained with the PBE, PBE0 and DDH functionals. We found
that electron-phonon interactions weakly affect the energy levels of the NV\textsuperscript{−} center, which
exhibit localized wavefunctions; they are instead more significant for the single Boron defect with delocalized wavefunctions. In the NV$^-$ center, the ZPR of the LUMO computed with the PBE functional is only $-35\,\text{meV}$ and that of the HOMO is negligible. In addition, the hybrid functionals PBE0 and DDH yield results similar to PBE. For the boron defect, with PBE (DDH) functional, the ZPRs of HOMO and LUMO are $111\,\text{meV}$ (121) and $126\,\text{meV}$ (241), respectively.

![Figure 4](image)

Figure 4: (a) The localized occupied state introduced by the nitrogen vacancy defect and (b) the delocalized unoccupied state introduced by the single boron vacancy defect. The wavefunctions are computed with the dielectric dependent hybrid functional. (c) and (d) illustrate the level ordering within the energy gap of diamond.

### 7 Conclusions

In this paper, we computed phonon frequencies and electron-phonon interaction at the level of hybrid density functional theory by using density matrix perturbation theory and by solving the Liouville equation. Using this approach, we obtained phonon frequencies and energy gap renormalizations for molecules and solids by evaluating the non-adiabatic full
Table 9: Computed energy levels (eV) and their zero-point renormalizations (eV) in NV\textsuperscript{−} center. Energy levels are referred to the HOMO energy level, and the labels of energy levels are given in Figure 4(c).

|        | PBE  | PBE0 | DDH  |
|--------|------|------|------|
|        | Level| ZPR  | Level| ZPR  | Level| ZPR  |
| LUMO   | 1.359| -0.035| 3.593| -0.033| 2.948| -0.033 |
| HOMO   | 0.000| 0.001| 0.000| 0.012| 0.000| 0.009 |
| HOMO-1 | -0.411| 0.012| -0.059| 0.004| -0.189| 0.008 |
| HOMO-2 | -0.924| 0.038| -0.942| 0.057| -0.952| 0.052 |

Table 10: Computed energy levels (eV) and their zero-point renormalizations (eV) in the boron defect. Energy levels are referred to the HOMO energy level, and the labels of energy levels are given in Figure 4(d).

|        | PBE  | PBE0 | DDH  |
|--------|------|------|------|
|        | Level| ZPR  | Level| ZPR  | Level| ZPR  |
| LUMO+2 | 4.061| -0.359| 6.109| -0.367| 5.517| -0.365 |
| LUMO+1 | 4.041| -0.361| 6.090| -0.368| 5.498| -0.367 |
| LUMO   | 0.137| 0.126| 1.389| 0.285| 1.027| 0.241 |
| HOMO   | 0.000| 0.111| 0.000| 0.126| 0.000| 0.121 |
| HOMO-1 | -0.278| 0.087| -0.319| 0.054| -0.308| 0.062 |
| HOMO-2 | -0.287| 0.089| -0.327| 0.104| -0.316| 0.100 |
frequency-dependent electron-phonon self-energies, thus circumventing the static and adiabatic approximations adopted in the AHC formalism, at no extra computational cost. We investigated the electronic properties of small molecules using LDA, PBE, B3LYP and PBE0 functionals. We also carried out calculations of the electronic structure of diamond with the PBE, PBE0 and DDH functionals, and found that the hybrid functionals PBE0/DDH noticeably improve the renormalized energy gap compared to experimental measurements. In addition, we studied the electron-phonon renormalizations of defects in diamond, and we concluded that electron-phonon effects are essential to fully understand the electronic structures of defects, especially those with relatively delocalized states.

In conclusion, computing electron-phonon interactions at the hybrid functional level of theory is a promising protocol to accurately describe the electronic structure of molecules and solids, and density matrix perturbation theory is a general technique that allows one to do so in an efficient and accurate manner, by evaluating non adiabatic and full frequency dependent electron-phonon self-energies.

Acknowledgement

This work was supported by the Midwest Integrated Center for Computational Materials (MICCoM) as part of the Computational Materials Sciences Program funded by the U.S. Department of Energy. This research used resources of the National Energy Research Scientific Computing Center (NERSC), a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231, resources of the Argonne Leadership Computing Facility, which is a DOE Office of Science User Facility supported under Contract DE-AC02-06CH11357, and resources of the University of Chicago Research Computing Center.
References

(1) Bloch, F. Über die quantenmechanik der elektronen in kristallgittern. Z. Phys. 1929, 52, 555–600.

(2) Bardeen, J.; Cooper, L. N.; Schrieffer, J. R. Microscopic Theory of Superconductivity. Phys. Rev. 1957, 106, 162–164.

(3) Giannozzi, P.; de Gironcoli, S.; Pavone, P.; Baroni, S. Ab ini tiocalculation of phonon dispersions in semiconductors. Phys. Rev. B 1991, 43, 7231–7242.

(4) Baroni, S.; de Gironcoli, S.; Corso, A. D.; Giannozzi, P. Phonons and related crystal properties from density-functional perturbation theory. Rev. Mod. Phys. 2001, 73, 515–562.

(5) Giustino, F.; Cohen, M. L.; Louie, S. G. Electron-phonon interaction using Wannier functions. Phys. Rev. B 2007, 76, 165108.

(6) Giustino, F. Electron-phonon interactions from first principles. Rev. Mod. Phys. 2017, 89, 015003.

(7) Antonius, G.; Poncé, S.; Boulanger, P.; Côté, M.; Gonze, X. Many-Body Effects on the Zero-Point Renormalization of the Band Structure. Phys. Rev. Lett. 2014, 112, 215501.

(8) Poncé, S.; Margine, E. R.; Giustino, F. Towards predictive many-body calculations of phonon-limited carrier mobilities in semiconductors. Physical Review B 2018, 97, 121201.

(9) Poncé, S.; Gillet, Y.; Janssen, J. L.; Marini, A.; Verstraete, M.; Gonze, X. Temperature dependence of the electronic structure of semiconductors and insulators. J. Chem. Phys. 2015, 143, 102813.
(10) McAvoy, R. L.; Govoni, M.; Galli, G. Coupling First-Principles Calculations of Electron–Electron and Electron–Phonon Scattering, and Applications to Carbon-Based Nanostructures. *J. Chem. Theory Comput.* **2018**, *14*, 6269–6275.

(11) Yang, H.; Govoni, M.; Kundu, A.; Galli, G. Combined First-Principles Calculations of Electron–Electron and Electron–Phonon Self-Energies in Condensed Systems. *Journal of Chemical Theory and Computation* **2021**, *17*, 7468–7476.

(12) Kundu, A.; Govoni, M.; Yang, H.; Ceriotti, M.; Gygi, F.; Galli, G. Quantum vibronic effects on the electronic properties of solid and molecular carbon. *Phys. Rev. Materials* **2021**, *5*, L070801.

(13) Fan, H. Y. Temperature Dependence of the Energy Gap in Monatomic Semiconductors. *Phys. Rev.* **1950**, *78*, 808–809.

(14) Fan, H. Y. Temperature dependence of the energy gap in semiconductors. *Phys. Rev.* **1951**, *82*, 900.

(15) Fröhlich, H.; Pelzer, H.; Zienau, S. XX. Properties of slow electrons in polar materials. *London, Edinburgh Dublin Philos. Mag. J. Sci.* **1950**, *41*, 221–242.

(16) Monserrat, B. Electron–phonon coupling from finite differences. *J. Phys.: Condens. Matter* **2018**, *30*, 083001.

(17) Engel, M.; Miranda, H.; Chaput, L.; Togo, A.; Verdi, C.; Marsman, M.; Kresse, G. Zero-point Renormalization of the Band Gap of Semiconductors and Insulators Using the PAW Method. 2022; [https://arxiv.org/abs/2205.04265](https://arxiv.org/abs/2205.04265).

(18) Karsai, F.; Engel, M.; Flage-Larsen, E.; Kresse, G. Electron–phonon coupling in semiconductors within the GW approximation. *New J. Phys.* **2018**, *20*, 123008.

(19) Monserrat, B.; Needs, R. Comparing electron-phonon coupling strength in diamond, silicon, and silicon carbide: First-principles study. *Phys. Rev. B* **2014**, *89*, 214304.
(20) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, A1133–A1138.

(21) Monserrat, B.; Engel, E. A.; Needs, R. J. Giant electron-phonon interactions in molecular crystals and the importance of nonquadratic coupling, *Physical Review B* **2015**, *92*, 140302.

(22) Kundu, A.; Govoni, M.; Galli, G. Unpublished. **2022**.

(23) Knoop, F.; Purcell, T. A.; Scheffler, M.; Carbogno, C. Anharmonicity measure for materials. *Physical Review Materials* **2020**, *4*, 083809.

(24) Allen, P. B.; Heine, V. Theory of the temperature dependence of electronic band structures. *J. Phys. C: Solid State Phys.* **1976**, *9*, 2305.

(25) Allen, P. B.; Cardona, M. Theory of the temperature dependence of the direct gap of germanium. *Phys. Rev. B* **1981**, *23*, 1495.

(26) Antonius, G.; Poncé, S.; Lantagne-Hurtubise, E.; Auclair, G.; Gonze, X.; Côté, M. Dynamical and anharmonic effects on the electron-phonon coupling and the zero-point renormalization of the electronic structure. *Phys. Rev. B* **2015**, *92*, 085137.

(27) Miglio, A.; Brousseau-Couture, V.; Godbout, E.; Antonius, G.; Chan, Y.-H.; Louie, S. G.; Côté, M.; Giantomassi, M.; Gonze, X. Predominance of non-adiabatic effects in zero-point renormalization of the electronic band gap. *npj Comput. Mater.* **2020**, *6*, 1–8.

(28) Li, W. Electrical transport limited by electron-phonon coupling from Boltzmann transport equation: An ab initio study of Si, Al, and MoS 2. *Physical Review B* **2015**, *92*, 075405.

(29) Poncé, S.; Margine, E. R.; Giustino, F. Towards predictive many-body calculations
of phonon-limited carrier mobilities in semiconductors. Physical Review B 2018, 97, 121201.

(30) Sio, W. H.; Verdi, C.; Poncé, S.; Giustino, F. Ab initio theory of polarons: Formalism and applications. Physical Review B 2019, 99, 235139.

(31) Sio, W. H.; Verdi, C.; Poncé, S.; Giustino, F. Polarons from first principles, without supercells. Physical Review Letters 2019, 122, 246403.

(32) Walker, B.; Saitta, A. M.; Gebauer, R.; Baroni, S. Efficient Approach to Time-Dependent Density-Functional Perturbation Theory for Optical Spectroscopy. Phys. Rev. Lett. 2006, 96, 113001.

(33) Rocca, D.; Lu, D.; Galli, G. Ab initio calculations of optical absorption spectra: Solution of the Bethe–Salpeter equation within density matrix perturbation theory. J. Chem. Phys. 2010, 133, 164109.

(34) Lanczos, C. An iteration method for the solution of the eigenvalue problem of linear differential and integral operators. J. Res. Natl. Bur. Stand. 1950, 45, 255.

(35) Rocca, D. Time-dependent density functional perturbation theory: new algorithms with applications to molecular spectra. Ph.D. thesis, Scuola Internazionale Superiore di Studi Avanzati, 2007.

(36) Rocca, D.; Gebauer, R.; Saad, Y.; Baroni, S. Turbo charging time-dependent density-functional theory with Lanczos chains. J. Chem. Phys. 2008, 128, 154105.

(37) Salpeter, E. E.; Bethe, H. A. A Relativistic Equation for Bound-State Problems. Phys. Rev. 1951, 84, 1232–1242.

(38) Strinati, G. Application of the Green’s functions method to the study of the optical properties of semiconductors. La Rivista del Nuovo Cimento (1978-1999) 1988, 11, 1–86.
(39) Rocca, D.; Ping, Y.; Gebauer, R.; Galli, G. Solution of the Bethe-Salpeter equation without empty electronic states: Application to the absorption spectra of bulk systems. *Phys. Rev. B* **2012**, *85*, 045116.

(40) Rocca, D. Random-phase approximation correlation energies from Lanczos chains and an optimal basis set: Theory and applications to the benzene dimer. *J. Chem. Phys.* **2014**, *140*, 18A501.

(41) Nguyen, N. L.; Ma, H.; Govoni, M.; Gygi, F.; Galli, G. Finite-Field Approach to Solving the Bethe-Salpeter Equation. *Phys. Rev. Lett.* **2019**, *122*, 237402.

(42) Born, M.; Oppenheimer, R. Zur Quantentheorie der Molekeln. *Ann. Phys. (Berlin)* **1927**, *389*, 457–484.

(43) Sternheimer, R. Electronic polarizabilities of ions from the Hartree-Fock wave functions. *Phys. Rev.* **1954**, *96*, 951.

(44) Ponc´e, S.; Antonius, G.; Gillet, Y.; Boulanger, P.; Janssen, J. L.; Marini, A.; Côté, M.; Gonze, X. Temperature dependence of electronic eigenenergies in the adiabatic harmonic approximation. *Phys. Rev. B* **2014**, *90*, 214304.

(45) Gonze, X.; Boulanger, P.; Côté, M. Theoretical approaches to the temperature and zero-point motion effects on the electronic band structure. *Ann. Phys.* **2011**, *523*, 168–178.

(46) Govoni, M.; Galli, G. Large Scale GW Calculations. *J. Chem. Theory Comput.* **2015**, *11*, 2680–2696.

(47) Perdew, J. P.; Ernzerhof, M.; Burke, K. Rationale for mixing exact exchange with density functional approximations. *J. Chem. Phys.* **1996**, *105*, 9982–9985.

(48) Schlipf, M.; Gygi, F. Optimization algorithm for the generation of ONCV pseudopotentials. *Comput. Phys. Commun.* **2015**, *196*, 36–44.
(49) Hamann, D. R. Optimized norm-conserving Vanderbilt pseudopotentials. *Phys. Rev. B* 2013, 88, 085117.

(50) Perdew, J. P.; Zunger, A. Self-interaction correction to density-functional approximations for many-electron systems. *Phys. Rev. B* 1981, 23, 5048.

(51) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* 1996, 77, 3865–3868.

(52) Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A* 1988, 38, 3098–3100.

(53) Becke, A. D. A new mixing of Hartree–Fock and local density-functional theories. *J. Chem. Phys.* 1993, 98, 1372–1377.

(54) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Physical review B* 1988, 37, 785.

(55) Shang, H.; Yang, J. Capturing the Electron–Phonon Renormalization in Molecules from First-Principles. *J. Phys. Chem. A* 2021, 125, 2682–2689.

(56) Tkatchenko, A.; Scheffler, M. Accurate Molecular Van Der Waals Interactions from Ground-State Electron Density and Free-Atom Reference Data. *Phys. Rev. Lett.* 2009, 102, 073005.

(57) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. Assessment of Gaussian-2 and density functional theories for the computation of ionization potentials and electron affinities. *J. Chem. Phys.* 1998, 109, 42–55.

(58) Skone, J. H.; Govoni, M.; Galli, G. Self-consistent hybrid functional for condensed systems. *Phys. Rev. B* 2014, 89, 195112.

(59) Skone, J. H.; Govoni, M.; Galli, G. Nonempirical range-separated hybrid functionals for solids and molecules. *Phys. Rev. B* 2016, 93, 235106.
(60) O’donnell, K. P.; Chen, X. Temperature dependence of semiconductor band gaps. *Appl. Phys. Lett.* **1991**, *58*, 2924–2926.

(61) Weber, J. R.; Koehl, W. F.; Varley, J. B.; Janotti, A.; Buckley, B. B.; de Walle, C. G. V.; Awschalom, D. D. Quantum computing with defects. *Proceedings of the National Academy of Sciences* **2010**, *107*, 8513–8518.

(62) Jin, Y.; Govoni, M.; Wolfowicz, G.; Sullivan, S. E.; Heremans, F. J.; Awschalom, D. D.; Galli, G. Photoluminescence spectra of point defects in semiconductors: Validation of first-principles calculations. *Phys. Rev. Materials* **2021**, *5*, 084603.

(63) Cao, Y.; Romero, J.; Olson, J. P.; Degroote, M.; Johnson, P. D.; Kieferová, M.; Kivlichan, I. D.; Menke, T.; Peropadre, B.; Sawaya, N. P. D.; Sim, S.; Veis, L.; Aspuru-Guzik, A. Quantum Chemistry in the Age of Quantum Computing. *Chemical Reviews* **2019**, *119*, 10856–10915, PMID: 31469277.

(64) Huang, B.; Govoni, M.; Galli, G. Simulating the Electronic Structure of Spin Defects on Quantum Computers. *PRX Quantum* **2022**, *3*, 010339.