Electron-phonon coupling as an order-one problem

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The coupling between electrons and phonons plays important roles in physics, chemistry and biology. However, the accurate calculation of the electron-phonon coupling constants is computationally expensive as it involves solving the Schrödinger equation for $O(N)$ nuclear configurations, where $N$ is the number of nuclei. Herein we show that by considering the forces on the nuclei caused by the addition or subtraction of an arbitrarily small electronic charge one may calculate the electron-phonon coupling constants from $O(1)$ solutions of the Schrödinger equation. We show that Janak’s theorem means that this procedure is exact within the density functional formalism. We demonstrate that the $O(1)$ approach produces numerically accurate results by calculating the electron-phonon coupling constants for a series of molecules ranging in size from H$_2$ to C$_6$. We use our approach to introduce a computationally fast approximation for the adiabatic ionisation potentials and electron affinities which is shown to be accurate for large molecules. We also show that our approach allows for the calculation isotope effects in $O(0)$ time and discuss the deuteration driven Mott transition in $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br.

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Electrons in condensed matter feel two forces: a direct Coulomb interaction between themselves and an Columbic interaction with the atomic nuclei. As the vibrations of the nuclei are quantised the interaction with the lattice takes the form of the electron-phonon (or electron-vibron) interaction. Electron-phonon interactions plays important roles across science from physics (electron-phonon interactions can give rise to superconductivity $\dagger$, spin and charge density waves $\ddagger$, polaron formation $\S$ and piezoelectricity $\dagger$, through chemistry (such as in electron transfer processes $\ddagger$, Jahn-Teller effects $\ddagger$, spectroscopy $\ddagger$, stereochemistry $\S$, activation of chemical reactions $\S$ and catalysis $\ddagger$) to biology (for example electron-phonon interactions play an important role in photoprotection $\ddagger$, photosynthesis $\ddagger$ and vision $\S$). It is therefore clear that one of the central tasks for condensed matter theory and theoretical chemistry is to accurately calculate electron-phonon coupling constants. However, until now, this has been a computationally expensive task.

The expense of calculating the electron-phonon coupling constants arises from the large number of phononic modes that need to be considered. For example, a (non-linear) molecule with $N$ atoms has $M = 3N - 6$ phononic modes. Within the Born-Oppenheimer approximation, the standard, frozen phonon, approach to calculating the electron-phonon coupling constants requires the electronic eigenstates to be calculated for $M$ nuclear configurations. Below we demonstrate how the number of calculations can be reduced from $M$ to 1 without increasing the difficulty of the electronic problem.

Let us begin by reviewing the basic problem of electron-phonon coupling in the semiclassical limit. In this limit the phonons are represented by harmonic oscillators, thus the Hamiltonian is

$$\mathcal{H} = \mathcal{H}_e^0 + \sum_i \left( \frac{p_i^2}{2m_i} + \frac{1}{2} k_i x_i^2 + \tilde{g}_i x_i n \right)$$

(1)

where $p_i$ is the momentum of the $i^{th}$ mode, $m_i$ is the effective mass of the $i^{th}$ mode, $k_i$ is the spring constant of the $i^{th}$ harmonic oscillator, $x_i$ is the displacement of the $i^{th}$ mode from its equilibrium position, the $\tilde{g}_i$ are the electron-phonon coupling constants, $n$ is the number of electrons and $\mathcal{H}_e^0$ is the Hamiltonian of the electrons in the absence of phonons. In what follows it will be useful to introduce dimensionless normal coordinates for the phonons given by $Q_i = x_i \sqrt{m_i \omega_i / \hbar}$, where $\omega_i = \sqrt{k_i / m_i}$ is the frequency of the phonon, dimensionless momenta, $P_i = p_i \sqrt{m_i / \hbar \omega_i}$, and dimensionless electron-phonon coupling constants, $g_i = \tilde{g}_i / \sqrt{2m_i \hbar \omega_i^3}$. Thus, the Hamiltonian may be written as

$$\mathcal{H} = \mathcal{H}_e^0 + \sum_i \left[ \frac{\hbar \omega_i}{2} (P_i^2 + Q_i^2) + \sqrt{2} g_i \hbar \omega_i Q_i n \right].$$

(2)

We may quantise this Hamiltonian by introducing the
Bosonic operators $\hat{a}_i^{\dagger}$ which annihilate (create) a phonon on the in the $i^{th}$ mode and the Fermionic operators $c_\mu$ which annihilate (create) an electron in the state $\mu$ such that $\hat{n}_\mu = c_\mu^{\dagger} c_\mu$, $\hat{Q}_i = \frac{1}{\sqrt{2}} (\hat{a}_i^{\dagger} + \hat{a}_i)$ and $\hat{P}_i = \frac{1}{\sqrt{2}} (\hat{a}_i^{\dagger} - \hat{a}_i)$. Thus the quantum Hamiltonian is

$$\hat{H} = \hat{H}_e^0 + \sum_i \hbar \omega_i \left( \hat{a}_i^{\dagger} \hat{a}_i + \frac{1}{2} \right) + \sum_{i\mu} g_{\mu i} \hbar \omega_i c_\mu^{\dagger} c_\mu (\hat{a}_i^{\dagger} + \hat{a}_i). \tag{3}$$

The coupling between the $i^{th}$ phononic mode and the $\mu^{th}$ electronic state is given by

$$g_{\mu i} = \frac{1}{\sqrt{2\hbar \omega_i}} \frac{\partial \lambda_\mu}{\partial Q_i} \tag{4}$$

where $\omega_i$ is the frequency of the mode and $\lambda_\mu$ is the energy of the $\mu^{th}$ electronic state. Therefore, to calculate the electron-phonon coupling constants via the frozen phonon method one begins by calculating the electronic structure and the normal modes of the system; one then makes a small displacement of the system along each normal coordinate, and thus calculates $\partial \lambda_\mu / \partial Q_i$. Therefore if there are $N$ normal modes $N$ such calculations must be performed. The frozen phonon method can be speeded up by the use of density functional perturbation theory (DFPT). \[1\] However, DFPT is an $O(N)$ technique, albeit with a smaller coefficient than the frozen phonon calculation. Below we present a new method to calculate $\partial \lambda_\mu / \partial Q_i$ in a single calculation.

Janak’s theorem \[10\] states that

$$\lambda_\mu = \frac{\partial E}{\partial n_\mu} \tag{5}$$

where $E$ is the total energy of the system and $n_\mu$ is the electronic occupancy of the state $\mu$. It is important to realise that, within the density functional formalism $n_\mu$ is not required to be an integer \[10\]. It follows from \[10\] and \[15\] that

$$g_{\mu i} = -\frac{1}{\sqrt{2\hbar \omega_i}} \lim_{\delta n_\mu \to 0} \frac{1}{\delta n_\mu} \left( \frac{\partial E}{\partial Q_i} \right)_{\delta n_\mu} \tag{6}$$

where $(\partial E / \partial Q_i)_0$ indicates that the derivative is taken after the charge is changed by $x$ relative to the charge of the initially optimised geometry. We have used the fact that for a (meta)stable geometry $(\partial E / \partial Q_i)_0 = 0$. Once the electronic structure is solved in the equilibrium geometry of the charge neutral system with a small change in the charge the forces on the molecule can be calculated using the Hellman-Feynman theorem and, as the dynamical matrix is already known from the calculation of phonon spectrum, the electron-phonon coupling constants can readily be calculated.

Conceptually it is useful to realise that in the frozen phonon and DFPT approaches one considers the problem from the point of view of the electrons. That is one calculates the electron-phonon coupling constants by making a small perturbation to nuclei and considering the resultant change on the electron. However, in the $O(1)$ approach one asks the question what happens to the nuclei when one puts a small additional charge in the system. In most cases one is only interested in the coupling of the phonons to the electronic states closest to the Fermi level, however, if one is interested in couplings to other states extensions of Janak’s theorem to other electronic states allows for the determination of these parameters straightforwardly within the $O(1)$ method.

Thus the main result of this letter is that using equation \[6\] the $g_i$ can be calculated by solving a single nuclear geometry. In the remainder of this work we present some benchmark calculations which show that equation \[6\] reproduces the values of the electron-phonon coupling constants calculated by the frozen phonon method for a number of small molecules. To do this we have implemented our scheme for calculating electron-phonon coupling constants in the Naval Research Laboratory Molecular Orbital Library (NRLMOL) \[11\] \[12\] \[13\] \[14\] \[15\] \[16\] [17]. Throughout we have used the Perdew-Burke-Ernzerhof (PBE) \[18\] exchange correlation functional.
In figure 2 we plot the calculated electron-phonon interactions for tetrathiafulvalene (TTF), tetra-cyanoquinodimethane (TCNQ), bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF), C\textsubscript{60} and a number of diatomic and other small molecules calculated by the frozen phonon method against the electron-phonon coupling constants calculated by our method. It can be seen that the approximation improves dramatically as the number of atoms in the molecule, \(N\), increases. The inset show the same data on a log-log scale, this suggests that the error in the approximation decreases as \(\Delta E \sim N^{-\alpha}\) with \(\alpha \sim 1.5 - 2\).

FIG. 2: The ionisation potentials and electron affinities of the molecules considered in Fig. 1. We plot the difference in energy, \(\Delta E\) between the correct result (within the PBE approximation) and the results from approximating the ionisation potential (electron affinity) by estimating the Hubbard \(U\) and relaxation energy from the \(\mathcal{O}(1)\) method. It can be seen that the approximation improves dramatically as the number of atoms in the molecule, \(N\), increases. The inset show the same data on a log-log scale, this suggests that the error in the approximation decreases as \(\Delta E \sim N^{-\alpha}\) with \(\alpha \sim 1.5 - 2\).

Because the calculation of electron-phonon coupling constants is now computationally inexpensive, it is possible to use the electron-phonon coupling to estimate other quantities. For example the adiabatic ionisation energy (or electron affinity) of a molecule, as opposed to the vertical ionisation energy (electron affinity) may be extracted from the information already calculated. To do this one determines the Hubbard \(U\) (a second derivative) from either the energy as a function of \(\mp \delta n_\mu\) and \(\mp 2\delta n_\mu\) or from the appropriate eigenvalue as a function of \(\mp \delta n_\mu\). As the electron-phonon coupling constants are known the adiabatic ionisation energy (electron affinity) can be calculated directly from Markus–Hush theory. In figure 2 we plot the difference between the adiabatic ionisation energies (electron affinities) calculated in this way and the correct result (within the PBE framework) for the molecules considered in Fig. 1 as a function of the the number of the atoms in the molecules. While for small molecules this approximation is not accurate, the results for the larger molecules are excellent. Clearly it is for larger molecules that this approximation is needed as the computational power required to relax the geometry grows with the size of the molecule.

It is important to stress that the calculation of the electron-phonon coupling constants is, in fact, intrinsically an \(\mathcal{O}(1)\) problem as the dynamical matrix and the forces calculated on the geometries used to calculate the dynamical matrix together with the eigenvalue changes determined during the course of these calculations contain all the information required to calculate the \(g_{\mu}\). However, significant computational complexities must be overcome to retrieve this information. Further, the calculated electron-phonon coupling is rather sensitive to the size of the displacement used in a frozen-phonon calculation. In general a simple criterion for the size of the displacement, \(\varepsilon = \sqrt{2\Delta / \hbar}\) where \(\Delta\) is a small energy, does not produce uniformly reliable results for all possible phonon frequencies in the frozen phonon calculations of the type discussed above. However, we have found that the results for the \(\mathcal{O}(1)\) method are highly insensitive to the value of the ‘small’ charge, \(\delta n_\mu\), used in the calculation.

Finally we note that the calculation of isotope effects is an \(\mathcal{O}(0)\) problem in our method, i.e. only trivial matrix manipulation and no further solutions of the Schrödinger equation are required to calculate the electron-phonon coupling constants as the isotopic masses are varied. This contrasts to the frozen-phonon method where, as the dynamical matrix and thus the normal modes change upon isotopic substitution, \(\mathcal{O}(N)\) additional calculations are required.

A particularly interesting isotope effect is observed in the superconductor \(\kappa\)-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. When the eight hydrogen atoms in the BEDT-TTF molecule are replaced by deuterium the ground state is found to be a Mott insulator. In the crystal the highest occupied molecular orbital (HOMO) of the BEDT-TTF molecule is doped with holes from the anion layer, therefore one expects that, in the small polaron limit, on deuteration, the bandwidth will change by a factor

\[
\frac{W_D}{W_H} = \frac{e^{-\sum_i |g_{iD}|}}{e^{-\sum_i |g_{iH}|}} = 0.97
\]

where \(W_D\) (\(W_H\)) is the bandwidth of the deuterated (hydrogenated) system and \(g_{iD}\) (\(g_{iH}\)) is the coupling between the \(i\)th mode and the HOMO in the deuterated
(hydrogenated) molecule. As both the deuterated and hydrogenated systems are very close to the Mott transition \[19\] we suggest that polarons may play a significant role in driving the Mott transition by deuteration.

In conclusion we have demonstrated that by considering the forces on the nuclei due to the addition or subtraction of an arbitrarily small electronic charge one may calculate the electron-phonon coupling constants as an $O(1)$ problem. This method is exact within the density functional formalism and was shown to be numerically accurate for a large number of small molecules. Note that, although we have only considered molecular systems in our numerical work this is no intrinsic limitation of this method which prevents it being applied to infinite systems.

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