

First-principles approach to the electron-phonon interaction

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We present a first-principles approach to the calculation of the electron-phonon interaction. This approach solves some theoretical difficulties in the standard derivation of the electron-phonon interaction. We do not make a Born-Oppenheimer approximation from the outset but transform the electronic coordinates to a frame attached to the nuclear framework. Subsequently coupled equations are derived which connect the nuclear density-density correlation function to the electron Green function, the screened interaction, and the vertex. This set of equations is completely equivalent to the full problem and therefore higher-order effects are systematically included. The derived equations are further compared to those obtained from the Fröhlich Hamiltonian. It is shown that careless use of this Hamiltonian leads to double counting but also insight is given why use of this Hamiltonian has led to many useful results. Finally a simple method is presented that allows for the inclusion of electron-phonon coupling within a density-functional context.

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I. INTRODUCTION

The interaction between electrons and phonons plays a key role in the description of many phenomena in solid-state physics. A wide variety of properties of solids depend on it, such as the resistivity of metals, the temperature dependence of optical spectra, and its most dramatic consequence is maybe that it gives rise to the phenomenon of superconductivity. Also in molecular systems coupling between nuclear and electronic motion leads to variety of physical effects, such as rotational magnetism.¹ A more spectacular example is given by molecules in strong laser fields where coupling between electronic and nuclear motion leads to the generation of even harmonics² where only odd harmonics are allowed within the Born-Oppenheimer approximation. In small molecules many of these phenomena can be studied using accurate wave-function methods. For solids methods of comparable accuracy are not yet available. However, owing to the development of computational techniques and resources, a clear increase can be observed in the number of systems and types of properties that can be calculated from first principles, i.e., without the need of adjustable or phenomenological parameters. These calculations are usually based on many-body Green-function theory or density-functional theory. Green-function theory^{3,4} has been used by many groups to calculate quasiparticle and excitonic properties of solids. Density-functional theory (DFT),⁵⁻⁷ on the other hand, has been mostly used to calculate ground-state properties but the number of applications that calculate excited-state properties using time-dependent density-functional theory⁸⁻¹⁰ (TDDFT) is increasing steadily.¹¹ By calculating Born-Oppenheimer surfaces, DFT also allows for an accurate determination of phonon frequencies, which are very close to the experimentally observed ones. In view of these developments it would seem a natural next step to combine DFT and Green-function methods to calculate phenomena that depend on the electron-phonon coupling in a first-principles manner. A first step towards this goal was taken by the group of Gross in which DFT and Green-function methods were used to calculate the critical temperature of model BCS

superconductors.¹² Inspired by these results we aimed to derive a general scheme that allows us to calculate properties that depend on the electron-phonon coupling in a first-principles manner, using Green-function and DFT methods. In doing so we found several conceptual difficulties with the derivations of the electron-phonon coupling within the standard literature. We subsequently found a derivation which resolves these difficulties and obtained a general computational scheme to calculate the electron-phonon coupling in which electrons and nuclei are treated fully quantum mechanically. This scheme could then be used to test the validity of model Hamiltonians. We furthermore found a way to incorporate electron-phonon interactions in TDDFT linear-response calculations.

The paper is divided as follows. In the second section we explain the difficulties associated with the standard derivations of the electron-phonon coupling. In the third section we derive the form of the Hamiltonian that forms a suitable starting point for our derivations. In the subsequent section we derive the coupled equations that form the central result of this work. The equations are very general and are valid for general molecules and solids. In the fifth section we show how the phonons affect the effective electron-electron interaction, thereby confirming results found in more phenomenological ways. In the sixth section we study the validity of the phenomenological Fröhlich Hamiltonian and show that careless use of this Hamiltonian leads to overscreening of the phonon frequencies. We subsequently show how electron-phonon coupling can be incorporated in TDDFT calculations. We finally present our results and conclusions.

II. DIFFICULTIES IN STANDARD DERIVATIONS OF THE ELECTRON-PHONON COUPLING

In this section we discuss some theoretical difficulties that arise in the standard derivations of the electron-phonon interaction. We start out from the complete Hamiltonian of the electron-nuclear system

$$\hat{H} = \hat{T}_n(\mathbf{R}) + \hat{W}_{nn}(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + \hat{W}_{ee}(\mathbf{r}) + \hat{W}_{en}(\mathbf{R}, \mathbf{r}), \quad (1)$$

where

$$\hat{T}_n = \sum_{\alpha=1}^{N_n} -\frac{\nabla_{\mathbf{R}_\alpha}^2}{2M_\alpha}, \quad (2)$$

$$\hat{T}_e = \sum_{i=1}^{N_e} -\frac{1}{2}\nabla_i^2, \quad (3)$$

$$\hat{W}_{nn} = \frac{1}{2} \sum_{\alpha \neq \beta}^{N_n} \frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|}, \quad (4)$$

$$\hat{W}_{ee} = \frac{1}{2} \sum_{i \neq j}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (5)$$

$$\hat{W}_{en} = -\sum_{i=1}^{N_e} \sum_{\alpha=1}^{N_n} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|.} \quad (6)$$

This Hamiltonian describes the interaction of N_e electrons with N_n nuclei of mass M_α and charge Z_α . Here \hat{T}_n and \hat{T}_e are the nuclear and electronic kinetic-energy operators. The operators \hat{W}_{ee} , \hat{W}_{nn} , and \hat{W}_{en} describe the electron-electron, nuclear-nuclear, and electron-nuclear interaction, respectively. Preceding any discussion of the electron-phonon interaction two approximations are made. First of all, the purely electronic problem is approximately solved for fixed positions of the atomic nuclei. The corresponding electronic Hamiltonian is

$$\hat{H}_e = \hat{T}_e(\mathbf{r}) + \hat{W}_{en}(\mathbf{r}, \mathbf{R}_0) + \hat{W}_{ee}(\mathbf{r}), \quad (7)$$

where \mathbf{r} denotes the electronic and \mathbf{R}_0 the nuclear positions. The kinetic energy is denoted by \hat{T}_e and the electron-electron and electron-nuclear interaction are denoted by \hat{W}_{ee} and \hat{W}_{en} . The corresponding Schrödinger equation is

$$\hat{H}_e \Phi_e(\mathbf{r}, \mathbf{R}_0) = \epsilon_e(\mathbf{R}_0) \Phi_e(\mathbf{r}, \mathbf{R}_0). \quad (8)$$

This problem is a complicated many-body problem in itself. Nevertheless, in the past decade large progress has been made towards a first-principles solution of this problem mainly using many-body Green-function methods. With help of the so-called *GW* approximation¹³⁻¹⁵ good band gaps and spectral functions of many solids can be obtained. With a subsequent solution of the Bethe-Salpeter equation also good description of optical spectra and excitonic effects is possible.¹¹ Second, to calculate the phonons the electronic energy must be known for several fixed positions of the nuclei from which we can calculate the Born-Oppenheimer (BO) energy surface. One usually writes, for a given solution Φ_e of the clamped nuclei problem, the wave function of the full problem as^{16,4}

$$\Psi(\mathbf{r}, \mathbf{R}) = \Phi_e(\mathbf{r}, \mathbf{R}) \chi(\mathbf{R}). \quad (9)$$

If one now optimizes $\chi(\mathbf{R})$ with help of the variational principle one obtains for χ the equation

$$[\hat{T}_n(\mathbf{R}) + \epsilon_{BO}(\mathbf{R})] \chi(\mathbf{R}) = E \chi(\mathbf{R}), \quad (10)$$

where the Born-Oppenheimer energy surface is defined as

$$\epsilon_{BO}(\mathbf{R}) = W_{nn}(\mathbf{R}) + \epsilon_e(\mathbf{R}) + \langle \Phi_e | \hat{T}_n | \Phi_e \rangle, \quad (11)$$

where in the last term only integration over electron coordinates is implied.⁴ It should be noted that in making the variation with respect to χ also mixed first-order derivative terms with respect to χ and Φ_e appear. However, for systems with time-reversal invariance (as we will be discussing) the wave functions can be chosen to be real and these terms are then readily seen to vanish.¹⁷ For the calculation of phonons it is now assumed that the BO surface has well-defined minima \mathbf{R}_0 and that the energy surface close to these minima is well described by a harmonic approximation. One introduces deviations from equilibrium and rewrites the Born-Oppenheimer equation for χ in terms of these coordinates. This gives a set of equations for coupled harmonic oscillators which can be diagonalized in terms of new normal coordinates \mathbf{Q} . In these coordinates we obtain a set of independent oscillators, known as phonons, which have characteristic frequencies Ω_i . The BO equation then attains the form

$$\begin{aligned} \hat{H}_{ph} \chi(\mathbf{Q}) &= \sum_{i=1}^{3N_n-6} \left(-\frac{1}{2} \frac{\partial^2}{\partial \mathbf{Q}_i^2} + \frac{1}{2} \Omega_i^2 \mathbf{Q}_i^2 \right) \chi(\mathbf{Q}) \\ &= [E - \epsilon_{BO}(\mathbf{R}_0)] \chi(\mathbf{Q}), \end{aligned} \quad (12)$$

where Ω_i is the phonon frequency corresponding to phonon coordinate \mathbf{Q}_i . These frequencies are obtained from the matrix of second derivatives of the energy at the minima of the BO surface. With the use of density-functional theory accurate energy surfaces and phonon spectra can be obtained in this way.¹⁸

The difficulties arise when we want to go beyond the Born-Oppenheimer approximation and calculate the effects of the electrons on the phonons and vice versa. To do this we must split up the original Hamiltonian into an electron part, a phonon part, and a remainder. This remainder is exactly the contribution that we are interested in. The usual approach is to simply replace the interaction between the nuclei and their kinetic energy by the phonon Hamiltonian and to express the Coulombic electron-nuclear attraction in terms of phonon coordinates. This yields⁴

$$\hat{H} = \hat{H}_{ph}(\mathbf{Q}) + \hat{T}_e(\mathbf{r}) + \hat{W}_{ee}(\mathbf{r}) + W_{en}(\mathbf{r}, \mathbf{Q}). \quad (13)$$

However, with this drastic step we obtain a Hamiltonian that is not equivalent to the full original Hamiltonian, since the electronic part of the Hamiltonian was already used to determine the phonon frequencies. We have therefore introduced an ill-defined amount of double counting. Another way to see that this Hamiltonian is not equivalent to the one we started with is that it is not invariant anymore under rotations and translations of all particles. This is because the coordinates \mathbf{Q} represent internal coordinates only, as six phonon coordinates that represent the center-of-mass motion and an overall rotation of the system have been eliminated (they have phonon frequency zero). If we regard our system as being finite, this means that we neglect rovibrational couplings that can have important effects in molecules. The derivation of the

Hamiltonian of Eq. (13) is therefore obviously not satisfactory. The question is therefore how to find a derivation of the electron-phonon coupling that does not suffer from these problems. An obvious way to avoid the double counting would be to avoid the Born-Oppenheimer approximation altogether and directly split the Hamiltonian in the following three terms:

$$\hat{H} = \hat{H}_e(\mathbf{r}) + \hat{H}_n(\mathbf{R}) + \hat{H}_{en}(\mathbf{r}, \mathbf{R}), \quad (14)$$

where, by adding and subtracting terms at nuclear equilibrium positions \mathbf{R}_0 , we have defined

$$\hat{H}_e(\mathbf{r}) = \hat{T}_e(\mathbf{r}) + \hat{W}_{ee}(\mathbf{r}) + \hat{W}_{en}(\mathbf{r}, \mathbf{R}_0) + \hat{W}_{nn}(\mathbf{R}_0), \quad (15)$$

$$\hat{H}_n(\mathbf{R}) = \hat{T}_n(\mathbf{R}) + \hat{W}_{nn}(\mathbf{R}) - \hat{W}_{nn}(\mathbf{R}_0), \quad (16)$$

$$\hat{H}_{en}(\mathbf{r}, \mathbf{R}) = \hat{W}_{en}(\mathbf{r}, \mathbf{R}) - \hat{W}_{en}(\mathbf{r}, \mathbf{R}_0). \quad (17)$$

The Hamiltonians H_e and \hat{H}_n are now purely electronic and purely nuclear Hamiltonians and could be used to define “bare” electrons and phonons. The strategy would then be to treat the term \hat{H}_{en} in perturbation theory. However, the zeroth-order Hamiltonian \hat{H}_n for the nuclei is (apart from the values of the masses and charges) identical to the Hamiltonian of the homogeneous electron gas and its only collective excitation mode is a plasmon mode. This Hamiltonian therefore gives a completely unrealistic phonon spectrum which completely lacks the acoustic modes and is a bad starting point for perturbation theory. One could, as is done in several standard texts,^{19,20} also consider a somewhat intermediate splitting in which ions, i.e., nuclei with rigid core electrons attached to them, are used as basic entities. This does, however, not solve the problem mentioned and introduces a further approximation and an arbitrariness in the definition of a core electron. Some works^{21,22} start out from the full Hamiltonian, Eq. (14), to derive expressions for some physical quantities but subsequently assume a periodic symmetry, in contradiction to the full translational and rotational invariance of Hamiltonian, Eq. (14), and use an expansion of \hat{H}_{en} in phonon coordinates which again assumes a split-up of the Hamiltonian as in Eq. (13) leading back to the double-counting problem. On the other hand, we know that the Born-Oppenheimer approximation gives phonon spectra that are in excellent agreement with experimental results. The Born-Oppenheimer Hamiltonian, Eq. (10), should therefore be a good starting point to discuss the electron-phonon interaction. This brings us back to the Hamiltonian of Eq. (13). In spite of the mentioned difficulties in its derivation, this model Hamiltonian has found many fruitful applications in the description of a wide range of effects where electron-phonon interaction plays a role. One usually expands \hat{W}_{en} to first order in \mathbf{Q} and treats this term, which is called the electron-phonon interaction, in perturbation theory. Often the electron-phonon interaction is parametrized and the parameters are determined either from experimental data or by physical considerations. This procedure accounts for a wide class of model Hamiltonians known as the Fröhlich Hamiltonian. Although these Hamiltonians can be very useful it is

not clear what their range of validity is and they are unsuitable for first-principles predictions.

We conclude that from a theoretical point of view there is a need for a first-principles approach to the electron-phonon interaction that avoids the introduction of model Hamiltonians. The aim of this work is therefore to provide a theoretical approach to the electron-phonon interaction that can be used in first-principles calculations and that does not suffer from the theoretical difficulties mentioned above. An important step in this direction has been taken by Hedin and Lundqvist.¹⁴ Rather than attempting to separate the Hamiltonian in an electron and a phonon part, they use the full Hamiltonian to derive several equations that couple the electron Green function, the screened interaction, the vertex, and the nuclear density-density correlation function. By iteration of these equations one obtains increasingly sophisticated approximations of all the many-body quantities involved. This approach also has the important theoretical advantage of allowing for an exact definition of phonons that is independent of the Born-Oppenheimer approximation. The phonon spectrum is then defined to be the spectrum corresponding to the spectral function of the exact nuclear density-density correlation function and is as such an experimental observable. The work of Hedin and Lundqvist has, however, two drawbacks. First of all, they derive their equations for classical nuclei, described by variables for which, at a certain point in the derivation, quantum-mechanical commutation relations must be used. Second, they start out from a Hamiltonian that has full translational and rotational symmetry and therefore the reduced quantities, such as the Green function, do not reflect the crystal symmetry. In this work we will remove these two drawbacks by dealing with quantum-mechanical nuclei from the outset and by referring the electronic coordinates to a body-fixed coordinate frame.

III. THE TRANSFORMED HAMILTONIAN

Let us start with a general remark on the full Hamiltonian of all electrons and nuclei of Eq. (1). This Hamiltonian is invariant under translations and rotations of all particles. This means that the ground-state wave function transforms under a representation of the translation and rotation group. Together with the inversion symmetry this implies that all one-body quantities such as the electron density are constant and that two-particle correlation functions, such as the electron Green function, only depend on the distance between their arguments. This is obviously not a convenient starting point to describe a periodic solid. The solution of the problem is obvious: we have to transform to a coordinate system that reflects the internal properties of the system. We will therefore carry out a coordinate transformation in which the electronic positions will be referred to a coordinate system attached to the nuclear framework.²³ In doing so we will assume that our system is finite but arbitrarily large so that our approach will be generally valid for molecules and solids. We first define the center of mass of the nuclei:

$$\mathbf{R}_{CMN} = \frac{1}{M_{nuc}} \sum_{\alpha}^{N_n} M_{\alpha} \mathbf{R}_{\alpha}, \quad (18)$$

where $M_{nuc} = \sum_{\alpha}^{N_n} M_{\alpha}$ is the total mass of all nuclei. The new electronic coordinates are then defined to be

$$\mathbf{r}'_i = \mathcal{R}(\alpha, \beta, \gamma)(\mathbf{r}_i - \mathbf{R}_{CMN}), \quad (19)$$

where \mathcal{R} is a rotation matrix and (α, β, γ) are Euler angles that specify the directions of the axes of the new coordinate system, which will be called the body-fixed frame (for details see Appendix A). The Euler angles are functions of the nuclear coordinates. The way they depend on the nuclear coordinates depends on the choice of our coordinate transformation. One could for instance choose the angles in such a way that the nuclear inertia tensor in terms of the rotated nuclear variables

$$\mathbf{R}'_i = \mathcal{R}(\alpha, \beta, \gamma)(\mathbf{R}_i - \mathbf{R}_{CMN}) \quad (20)$$

becomes diagonal, where the nuclear inertia tensor is given by

$$I_{pq}(\mathbf{R}) = \sum_{\alpha}^{N_n} M_{\alpha} (|\mathbf{R}_{\alpha}|^2 \delta_{pq} - R_p^{\alpha} R_q^{\alpha}). \quad (21)$$

Note that if we write out a particle coordinate we use the particle label as a superscript, i.e., $\mathbf{R}_{\alpha} = (R_1^{\alpha}, R_2^{\alpha}, R_3^{\alpha})$. This way of determining the Euler angles is a common choice in nuclear physics.^{24–26} However, for the description of phonons it is more appropriate to make a choice which minimizes the coupling between rotational and vibrational motion. This is most conveniently done by using the so-called Eckart conditions^{27,28} that are commonly used in molecular physics to decouple nuclear and electronic motion.^{29–35} However, since they are rarely used in solid-state physics we will give a brief description of these conditions. Let $\mathbf{R}_{0,\alpha}$ be the nuclear positions that minimize the total energy within the Born-Oppenheimer approximation. These quantities will be used as parameters in our coordinate transformation. We choose them in such a way that

$$\sum_{\alpha}^{N_n} M_{\alpha} \mathbf{R}_{0,\alpha} = 0, \quad (22)$$

i.e., we refer these positions to their center of mass. We further choose these quantities in such a way that the inertia tensor $I_{pq}(\mathbf{R}_0)$ of Eq. (21) evaluated for these equilibrium positions becomes diagonal. Then we define the Euler angles as function of the nuclear coordinates \mathbf{R}_{α} by the following implicit equation:

$$0 = \sum_{\alpha}^{N_n} M_{\alpha} \mathbf{R}_{0,\alpha} \times \mathbf{R}'_{\alpha}. \quad (23)$$

It is important to realize that the numbers $\mathbf{R}_{0,\alpha}$ are not variables but just conveniently chosen parameters in a coordinate transformation. The Coulomb potential in the electron-nuclear interaction now acquires the form

$$\begin{aligned} \frac{1}{|\mathbf{r} - \mathbf{R}|} &= \frac{1}{|\mathbf{R}_{CMN} + \mathcal{R}(\alpha, \beta, \gamma)^{-1} \mathbf{r}' - \mathbf{R}|} \\ &= \frac{1}{|\mathcal{R}(\alpha, \beta, \gamma)(\mathbf{R} - \mathbf{R}_{CMN}) - \mathbf{r}'|} = \frac{1}{|\mathbf{R}' - \mathbf{r}'|}, \end{aligned} \quad (24)$$

where one has to keep in mind that the Euler angles (α, β, γ) are functions of the nuclear coordinates $(\mathbf{R}_1, \dots, \mathbf{R}_{N_n})$. The electron-nuclear interaction in the body-fixed frame is now invariant under translations and rotations of the nuclear coordinates. This is readily seen. First of all the quantities $\mathbf{R}_{\alpha} - \mathbf{R}_{CMN}$ are invariant under a translation $\mathbf{R}_{\alpha} \rightarrow \mathbf{R}_{\alpha} + \mathbf{a}$ and hence the Euler angles are invariant as well. Let us therefore consider rotations. Suppose we have a set of Euler angles corresponding to nuclear positions \mathbf{R}_{α} . Let us now apply a rotation O to these coordinates, i.e., we have new coordinates $\tilde{\mathbf{R}}_{\alpha} = O\mathbf{R}_{\alpha}$. For these rotated coordinates we have new Euler angles $(\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma})$ determined by the Eckart conditions

$$0 = \sum_{\alpha}^N M_{\alpha} \mathbf{R}_{0,\alpha} \times \mathcal{R}(\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}) O(\mathbf{R}_{\alpha} - \mathbf{R}_{CMN}). \quad (25)$$

Now since \mathcal{R} times O is again a rotation, it can be parametrized by Euler angles, i.e., we can write

$$\mathcal{R}(\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}) O = \mathcal{R}(\bar{\alpha}, \bar{\beta}, \bar{\gamma}) \quad (26)$$

for some Euler angles $(\bar{\alpha}, \bar{\beta}, \bar{\gamma})$. Now since the Eckart conditions determine the Euler angles uniquely we must have $(\bar{\alpha}, \bar{\beta}, \bar{\gamma}) = (\alpha, \beta, \gamma)$ and we find

$$\mathcal{R}(\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma})(\tilde{\mathbf{R}}_i - \tilde{\mathbf{R}}_{CMN}) = \mathcal{R}(\alpha, \beta, \gamma)(\mathbf{R}_i - \mathbf{R}_{CMN}). \quad (27)$$

We can therefore conclude that the coordinates \mathbf{R}'_{α} are so-called internal or shape coordinates that are invariant under rotations and translations of the nuclear framework, i.e., they satisfy

$$\mathbf{R}'_{\alpha}(O\mathbf{R} + \mathbf{a}) = \mathbf{R}'_{\alpha}(\mathbf{R}). \quad (28)$$

(A very elegant discussion of such coordinates is given in Ref. 32.) Therefore the potential that the electrons in the body-fixed frame experience from the nuclei is invariant under rotation and translation of the nuclear coordinates. This is, of course, exactly the purpose of a body-fixed frame. Let us now turn to the other terms in Hamiltonian. One can also see that the electron-electron repulsion and the electronic kinetic energy retain the same form in the primed as in the unprimed coordinates. This is simply because \mathcal{R} represents a rotation in which the Euler angles only depend on the nuclear coordinates and are independent of the electronic coordinates. However, for the same reason extra terms will appear in the nuclear kinetic energy. These terms have a physical origin. If all nuclei vibrate around their equilibrium position then also the axes of the body-fixed frame will vibrate and therefore we are viewing the electrons from a moving frame in which fictitious or Coriolis forces appear. In a diatomic molecule, for instance, this means that there is a

coupling between rotational and vibrational modes. For a solid we will show in Appendix C that such rovibrational terms are usually vanishingly small. The transformed nuclear kinetic terms become

$$\hat{T}'_n = \sum_{\alpha}^{N_n} \frac{\bar{\nabla}_{\mathbf{R}_{\alpha}}^2}{2M_{\alpha}}, \quad (29)$$

where we defined

$$\bar{\nabla}_{\mathbf{R}_{\alpha}} = \nabla_{\mathbf{R}_{\alpha}} + \sum_j^{N_e} \frac{\partial \mathbf{r}'_j}{\partial \mathbf{R}_{\alpha}} \nabla_{\mathbf{r}'_j}. \quad (30)$$

We define the mass-polarization and Coriolis terms now by

$$\hat{T}_{MPC} = \hat{T}'_n - \hat{T}_n. \quad (31)$$

We have now completely specified our coordinate system and Hamiltonian. In order not to overcrowd our formulas with superscripts we will from now on drop all primes from the electronic variables. In the new coordinate system the Hamiltonian is

$$\hat{H} = \hat{H}_n + \hat{H}_e + \hat{T}_{MPC} + \hat{W}_{en}, \quad (32)$$

where

$$\hat{H}_e = \sum_{i=1}^{N_e} -\frac{1}{2} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (33)$$

$$\hat{H}_n = \sum_{\alpha=1}^{N_n} -\frac{\nabla_{\mathbf{R}_{\alpha}}^2}{2M_{\alpha}} + \frac{1}{2} \sum_{\alpha, \beta}^{N_n} \frac{Z_{\alpha} Z_{\beta}}{|\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|}, \quad (34)$$

$$\hat{W}_{en} = \sum_{i=1}^{N_n} \sum_{j=1}^{N_e} \frac{-Z_i}{|\mathcal{R}(\alpha, \beta, \gamma)(\mathbf{R}_i - \mathbf{R}_{CMN}) - \mathbf{r}_j|}. \quad (35)$$

The term $\hat{T}_{MPC} = \hat{T}_{MP} + \hat{T}_C$ is the sum of a Coriolis part \hat{T}_C and mass-polarization part \hat{T}_{MP} which have the form (see Appendix B)

$$\hat{T}_{MP} = \sum_{r=1}^3 (\mu_r^{\dagger} + \mu_r) P_{e,r} + \sum_{rs=1}^3 \beta_{rs} P_{e,r} P_{e,s}, \quad (36)$$

$$\hat{T}_C = \sum_{r=1}^3 (\nu_r^{\dagger} + \nu_r) L_{e,r} + \sum_{rs=1}^3 \alpha_{rs} L_{e,r} L_{e,s}, \quad (37)$$

where \mathbf{P}_e and \mathbf{L}_e are the total electronic momentum and angular momentum. The quantities μ , ν , α , β are functions of the nuclear coordinates and are further specified in Appendix B where it is shown that μ and β are inversely proportional to the total nuclear mass. The form of these equations is independent of the way the body-fixed frame is chosen. So far our derivations are valid for any system of electrons and nuclei, i.e., ranging from small molecules to solids. Let us now specify that we are dealing with solids. Obviously then the mass-polarization terms can be neglected since they are inversely proportional to the total nuclear mass. If we use the Eckart conditions in the specification of the Euler angles then also the Coriolis terms in \hat{T}_C will be negligible. In Appendix

C it will be demonstrated that in that case these terms are inversely proportional to the diagonal elements $I_{qq}(\mathbf{R}_0)$ of the inertia tensor and therefore very small for large systems. This is a direct consequence of the Eckart conditions and this is exactly why these conditions are so suitable to define the transformation to the body-fixed frame. By neglect of the mass-polarization and Coriolis terms we have now obtained a Hamiltonian of the same form as the original Hamiltonian of Eq. (1) with the exception of the electron-nuclear attraction term which appears in the form of Eq. (35) and breaks the full translational and rotational symmetry. This Hamiltonian will now be used as a basis of our derivations.

IV. DERIVATION OF SELF-CONSISTENT EQUATIONS

We will start our derivations from the Hamiltonian derived in the preceding section. For the moment we will neglect the Coriolis and mass-polarization terms. The justification of this for solids is, as mentioned before, explained in more detail in Appendix C. In the case of molecular systems these extra terms are often incorporated later using perturbation theory.³³ With this approximation the transformed Hamiltonian in second quantization is given by

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{W}_{ee} + \hat{W}_{nn} + \hat{W}_{en}, \quad (38)$$

where

$$\hat{T}_e = -\frac{1}{2} \int d\mathbf{x} \hat{\psi}^{\dagger}(\mathbf{x}) \nabla^2 \hat{\psi}(\mathbf{x}), \quad (39)$$

$$\hat{W}_{ee} = \frac{1}{2} \int d\mathbf{x} d\mathbf{x}' \hat{\psi}^{\dagger}(\mathbf{x}) \hat{\psi}^{\dagger}(\mathbf{x}') \hat{\psi}(\mathbf{x}') \hat{\psi}(\mathbf{x}) w(\mathbf{r}, \mathbf{r}'), \quad (40)$$

$$\hat{W}_{en} = \int d\mathbf{x} dV \hat{\psi}^{\dagger}(\mathbf{x}) \hat{\psi}(\mathbf{x}) \hat{\Gamma}(\mathbf{R}_1 \cdots \mathbf{R}_{N_n}) \sum_i \frac{-Z_i}{|\mathbf{R}'_i - \mathbf{r}|}, \quad (41)$$

where $\mathbf{x} = (\mathbf{r}, \sigma)$ denotes a space-spin coordinate and \mathbf{R}'_i is a function of the coordinates \mathbf{R}_i as given by Eq. (20). The electronic field operators satisfy the usual anticommutation relations.^{4,19} We further defined the nuclear density matrix

$$\hat{\Gamma}(\mathbf{R}_1 \cdots \mathbf{R}_{N_n}) = \sum_{\sigma_1, \dots, \sigma_{N_n}} \hat{\phi}_1^{\dagger}(\mathbf{R}_1 \sigma_1) \cdots \hat{\phi}_{N_n}^{\dagger}(\mathbf{R}_{N_n} \sigma_{N_n}) \times \hat{\phi}_{N_n}(\mathbf{R}_{N_n} \sigma_{N_n}) \cdots \hat{\phi}_1(\mathbf{R}_1 \sigma_1), \quad (42)$$

where $\hat{\phi}_i^{\dagger}(\mathbf{R}\sigma)$ and $\hat{\phi}_i(\mathbf{R}\sigma)$ are nuclear creation and annihilation operators for nucleus i and where we summed over all nuclear spin variables σ_i . We further defined

$$dV = d\mathbf{R}_1 \cdots d\mathbf{R}_{N_n}. \quad (43)$$

The reason that in the electron-nuclear interaction \hat{W}_{en} a density matrix appears is a consequence of our transformation to the body-fixed frame which makes, as mentioned before, \mathbf{R}'_i a function of all the coordinates \mathbf{R}_i . The operators \hat{T}_n and \hat{W}_{nn} are not written out in second-quantization form here.

The only property of these operators that we will need in this section is that they commute with any operator that depends only on electronic coordinates. Note that we have not defined the commutation relations for the nuclear creation and annihilation operators $\hat{\phi}_i^\dagger$ and $\hat{\phi}_i$. The reason is that this does not only depend on the type of nucleus, i.e., either bosonic or fermionic, but also on the way the body-fixed frame is defined. For instance, if we choose the diagonalization of the inertia tensor to define the body-fixed frame then the Euler angles are defined by a constraint that is invariant under permutations of particles of the same type. In that case $\hat{\phi}_i^\dagger$ and $\hat{\phi}_i$ will have either bosonic or fermionic commutation relations. However, if we define the body-fixed frame using the Eckart conditions the commutation relations for $\hat{\phi}_i^\dagger$ and $\hat{\phi}_i$ will be more complicated. The reason is that the Eckart conditions are not invariant under permutations of particles of the same type as a consequence of the introduction of equilibrium positions $\mathbf{R}_{i,0}$. The true permutational symmetry of the system is then masked by the choice of our coordinate system, but is of course not changed. Luckily we will not have to use the commutation relations of the nuclear creation and annihilation operators in this section and our results will be valid for any choice of body-fixed frame (apart from the question whether or not the Coriolis terms are negligible). From a more physical point of view one might argue that in a solid in equilibrium the exchange probability of two nuclei is very small so that we may regard them as distinguishable particles and thereby simplify the mentioned problem. However, since in our analysis there is no absolute need for such approximations we refrain from doing so. For further discussions on this point for molecules we refer to Refs. 34 and 35.

We now define a potential operator by

$$\hat{V}_n(\mathbf{r}) = \int dV \hat{\Gamma}(\mathbf{R}_1 \cdots \mathbf{R}_{N_n}) \sum_{i=1}^{N_n} \frac{Z_i}{|\mathbf{R}'_i - \mathbf{r}|}. \quad (44)$$

The expectation value of this operator is the Coulomb potential due to the nuclei felt by the electrons in the body-fixed frame. We further define a nuclear density operator by

$$\hat{N}(\mathbf{r}) = \frac{1}{4\pi} \nabla^2 \hat{V}_n(\mathbf{r}) = \int dV \hat{\Gamma}(\mathbf{R}_1 \cdots \mathbf{R}_{N_n}) \sum_{i=1}^{N_n} Z_i \delta(\mathbf{r} - \mathbf{R}'_i). \quad (45)$$

The expectation value of this operator is the nuclear charge distribution in body-fixed frame coordinates that gives rise to the Hartree potential felt by the electrons. This is a smeared out density of nuclei, as opposed to the δ peaks that would arise from a clamped nuclei approximation. One clearly sees from Eq. (45) that if we have the full density matrix Γ we can rotate the nuclei to the body-fixed frame after calculation of the density matrix, rather than doing the coordinate transformation in the Hamiltonian. The electronic density is as usual given by the expectation value of the density operator

$$\hat{n}(\mathbf{r}) = \sum_{\sigma} \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x}). \quad (46)$$

We further define a total density by

$$\hat{\rho}(\mathbf{r}) = \hat{n}(\mathbf{r}) - \hat{N}(\mathbf{r}). \quad (47)$$

With the above definitions the electron-nuclear interaction can be simplified to

$$\hat{W}_{en} = - \int d^3r d^3\mathbf{R} \frac{\hat{n}(\mathbf{r}) \hat{N}(\mathbf{R})}{|\mathbf{r} - \mathbf{R}|}. \quad (48)$$

If we evaluate the expectation value of this operator in the mean-field sense, we see that the electron cloud now interacts with a smeared out nuclear charge, rather than δ peaks as in the clamped nuclei approximation. This reflects the quantum treatment of the nuclei.

Now we will follow the derivation of the Hedin equations¹³ along the lines of Hedin and Lundqvist.¹⁴ The strategy is to obtain self-consistent equations for well-defined objects such as the electron Green function, the screened interaction, and the vertex function. The advantage of this approach is that it does not depend on any perturbation expansion of the Hamiltonian. Approximations are made in the final self-consistent equations that contain physical quantities such as dressed electron and phonon propagators. The self-consistent equations are derived by the functional differentiation method. For this purpose we define an auxiliary external field $\varphi(\mathbf{r}t)$ coupling to the total charge $\hat{\rho}$. Our Hamiltonian therefore becomes

$$\begin{aligned} \hat{H} = & \hat{T}_n + \hat{W}_{nn} - \frac{1}{2} \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) \nabla^2 \hat{\psi}(\mathbf{x}) \\ & + \frac{1}{2} \int d\mathbf{x} d\mathbf{x}' \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}') \hat{\psi}(\mathbf{x}) w(\mathbf{r}, \mathbf{r}') \\ & - \int d^3r d^3\mathbf{R} \frac{\hat{n}(\mathbf{r}) \hat{N}(\mathbf{R})}{|\mathbf{r} - \mathbf{R}|} + \int d^3r \hat{\rho}(\mathbf{r}) \varphi(\mathbf{r}t). \end{aligned} \quad (49)$$

This is the Hamiltonian we will use for all our derivations. First we derive the equation of motion of the electronic field operator $\hat{\psi}$ in the Heisenberg picture (we use the same notation as in the paper by Hedin¹³),

$$\hat{\psi}_H(\mathbf{x}t) = V(-T_0, t) \hat{\psi}(\mathbf{x}) V(t, -T_0), \quad (50)$$

where $-T_0$ is an initial time and

$$V(t_2, t_1) = T \exp \left(-i \int_{t_1}^{t_2} \hat{H}(t) dt \right) \quad (51)$$

is the evolution operator [we use the time ordering since $\hat{H}(t)$ contains the explicitly time-dependent external field $\varphi(\mathbf{r}t)$]. The equation of motion of $\hat{\psi}_H$ follows from

$$i \partial_t \hat{\psi}_H(\mathbf{x}t) = [\hat{\psi}_H(\mathbf{x}t), \hat{H}(t)]. \quad (52)$$

Working out the commutator yields

$$i \partial_t \hat{\psi}_H(\mathbf{x}t) = \left(-\frac{1}{2} \nabla^2 + \varphi(\mathbf{r}t) + \int d^3r' \frac{\hat{\rho}_H(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} \right) \hat{\psi}_H(\mathbf{x}t), \quad (53)$$

where we used that $\hat{\psi}_H$ commutes with all nuclear operators. If we define the time-ordered product as usual,

$$\begin{aligned} T[\hat{\psi}_H(\mathbf{x}t)\hat{\psi}_H^\dagger(\mathbf{x}'t')] &= \theta(t-t')\hat{\psi}_H(\mathbf{x}t)\hat{\psi}_H^\dagger(\mathbf{x}'t') \\ &\quad - \theta(t'-t)\hat{\psi}_H^\dagger(\mathbf{x}'t')\hat{\psi}_H(\mathbf{x}t), \end{aligned} \quad (54)$$

where θ is the Heaviside function, then we obtain using the commutation relations of the field operators and $d\theta(t)/dt = \delta(t)$

$$\begin{aligned} &\left(i\partial_t + \frac{1}{2}\nabla^2 - \varphi(\mathbf{r}t)\right)T[\hat{\psi}_H(\mathbf{x}t)\hat{\psi}_H^\dagger(\mathbf{x}'t')] \\ &= i\delta(\mathbf{x}-\mathbf{x}')\delta(t-t') + \int d^3r' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \\ &\quad \times T[\hat{\rho}_H(\mathbf{r}'t)\hat{\psi}_H(\mathbf{x}t)\hat{\psi}_H^\dagger(\mathbf{x}'t')]. \end{aligned} \quad (55)$$

The equation of motion for $\hat{\psi}_H$ immediately yields an equation of motion for the electron Green function defined as

$$\begin{aligned} G(\mathbf{x}t, \mathbf{x}'t') &= -i \frac{\langle \Psi | U(-T_0, T_0) V(T_0, -T_0) T[\hat{\psi}_H(\mathbf{x}t)\hat{\psi}_H^\dagger(\mathbf{x}'t')] | \Psi \rangle}{\langle \Psi | U(-T_0, T_0) V(T_0, -T_0) | \Psi \rangle}. \end{aligned}$$

Here U is the evolution operator in absence of the external field φ . This means that for $\varphi=0$ the definition of the Green function reduces to the usual one. Note that we here work with time-ordered Green functions in the zero-temperature formalism. If one would be interested in finite temperature or nonequilibrium phenomena our derivations can be readily extended by use of the Matsubara technique³ or Keldysh Green functions.^{36,37} Now the functional derivative of V with respect to φ is

$$\frac{\delta V(t, t')}{\delta \varphi(\mathbf{r}_1 t_1)} = -i \text{sgn}(t-t') V(t, t_1) \hat{\rho}(\mathbf{r}_1) V(t_1, t') \quad (56)$$

if t_1 is inside the time interval determined by t and t' , otherwise $\delta V/\delta \varphi$ is zero. Using this expression we can readily prove the following equation:

$$\begin{aligned} &\frac{\delta}{\delta \varphi(\bar{3})} V(T_0, -T_0) T[\hat{\psi}_H(1)\hat{\psi}_H^\dagger(2)] \\ &= -i V(T_0, -T_0) T[\hat{\rho}_H(3)\hat{\psi}_H(1)\hat{\psi}_H^\dagger(2)], \end{aligned} \quad (57)$$

where we used the short notation $i = (\mathbf{x}_i, t_i)$. If the spin variable is left out we write $\bar{i} = (\mathbf{r}_i, t_i)$. With this equation we obtain the following equation for the electron Green function:

$$\begin{aligned} &\left(i\partial_{t_1} + \frac{1}{2}\nabla_1^2 - V(\bar{1})\right)G(1,2) \\ &= \delta(1-2) + i \int d\bar{3} w(\bar{1}^+, \bar{3}) \frac{\delta G(1,2)}{\delta \varphi(\bar{3})}, \end{aligned} \quad (58)$$

where $1^+ = (\mathbf{r}_1, t_1 + \Delta)$ with Δ a positive infinitesimal and $w(\bar{1}, \bar{2}) = \delta(t_1 - t_2)/|\mathbf{r}_1 - \mathbf{r}_2|$. The potential V that appears in the equation above is

$$V(\bar{1}) = \varphi(\bar{1}) + \int d\bar{3} w(\bar{1}, \bar{3}) \langle \hat{\rho}_H(\bar{3}) \rangle, \quad (59)$$

where we used the notation

$$\langle \hat{A} \rangle = \frac{\langle \Psi | U(-T_0, T_0) V(T_0, -T_0) \hat{A} | \Psi \rangle}{\langle \Psi | U(-T_0, T_0) V(T_0, -T_0) | \Psi \rangle}. \quad (60)$$

The potential $V(\bar{1})$ therefore corresponds to the external potential and the Hartree potential due to the electronic and nuclear charge distributions. Now we define the self-energy operator Σ by the equation

$$\begin{aligned} &\left(i\partial_{t_1} + \frac{1}{2}\nabla_1^2 - V(\bar{1})\right)G(1,2) \\ &= \delta(1-2) + \int d\bar{3} \Sigma(1,3)G(3,2). \end{aligned} \quad (61)$$

From the definition of the inverse Green function

$$\int d\bar{3} G(1,3)G^{-1}(3,2) = \delta(1-2) \quad (62)$$

follows the identity

$$\frac{\delta G(1,2)}{\delta \varphi(\bar{3})} = - \int d\bar{4} d\bar{5} G(1,4) \frac{\delta G^{-1}(4,5)}{\delta \varphi(\bar{3})} G(5,2). \quad (63)$$

We therefore see that we can write Σ as

$$\Sigma(1,2) = -i \int d\bar{3} d\bar{4} w(\bar{1}^+, \bar{3}) G(1,4) \frac{\delta G^{-1}(4,2)}{\delta \varphi(\bar{3})}. \quad (64)$$

In the next step we define a dielectric function ϵ and a screened interaction W by

$$\epsilon^{-1}(\bar{1}, \bar{2}) = \frac{\delta V(\bar{1})}{\delta \varphi(\bar{2})} = \delta(\bar{1}-\bar{2}) + \int d\bar{3} w(\bar{1}, \bar{3}) \frac{\delta \langle \hat{\rho}(\bar{3}) \rangle}{\delta \varphi(\bar{2})}, \quad (65)$$

$$W(\bar{1}, \bar{2}) = \int d\bar{3} w(\bar{1}, \bar{3}) \epsilon^{-1}(\bar{2}, \bar{3}). \quad (66)$$

The dielectric function measures changes in the effective potential due to charge changes induced by the external field. Note that it contains both changes in the electronic and nuclear charge densities. We wish to study them separately. The electronic polarization is defined as the electronic charge response due to the effective field

$$P_e(\bar{1}, \bar{2}) = \frac{\delta \langle \hat{n}(\bar{1}) \rangle}{\delta V(\bar{2})}. \quad (67)$$

The electronic charge can also be calculated directly from the Green function

$$\langle \hat{n}(\bar{3}) \rangle = -i \sum_{\sigma_3} G(3,3^+). \quad (68)$$

We therefore find

$$\begin{aligned} P_e(\bar{1}, \bar{2}) &= -i \sum_{\sigma_1} \frac{\delta G(1,1^+)}{\delta V(\bar{2})} \\ &= i \sum_{\sigma_1} \int d3d4 G(1,3)G(4,1) \frac{\delta G^{-1}(3,4)}{\delta V(\bar{2})}. \end{aligned} \quad (69)$$

If we define the vertex function Γ by

$$\Gamma(34; \bar{2}) = - \frac{\delta G^{-1}(3,4)}{\delta V(\bar{2})} \quad (70)$$

we obtain

$$P_e(\bar{1}, \bar{2}) = -i \sum_{\sigma_1} \int d3d4 G(1,3)G(4,1)\Gamma(34; \bar{2}). \quad (71)$$

This is the first one of Hedin's equations. A second one follows immediately from the definition of the self-energy and the screened interaction,

$$\begin{aligned} \Sigma(1,2) &= -i \int d\bar{3}d4d\bar{5} w(\bar{1}^+, \bar{3})G(1,4) \frac{\delta G^{-1}(4,2)}{\delta V(\bar{5})} \frac{\delta V(\bar{5})}{\delta \varphi(\bar{3})} \\ &= i \int d4d\bar{5} G(1,4)W(\bar{1}^+, \bar{5})\Gamma(42; \bar{5}). \end{aligned} \quad (72)$$

A third equation follows directly from the definition of the vertex function,

$$\begin{aligned} \Gamma(12; \bar{3}) &= \delta(1-2)\delta(\bar{1}-\bar{3}) + \frac{\delta \Sigma(1,2)}{\delta V(\bar{3})} \\ &= \delta(1-2)\delta(\bar{1}-\bar{3}) + \int d4d5 \frac{\delta \Sigma(1,2)}{\delta G(4,5)} \frac{\delta G(4,5)}{\delta V(\bar{3})} \\ &= \delta(1-2)\delta(\bar{1}-\bar{3}) \\ &\quad + \int d4d5d6d7 \frac{\delta \Sigma(1,2)}{\delta G(4,5)} G(4,6)G(7,5)\Gamma(67; \bar{3}). \end{aligned} \quad (73)$$

This yields an integral equation for the vertex function. In order to proceed we investigate the relation between W and P_e . From the definition of W we see that

$$W(\bar{1}, \bar{2}) = w(\bar{1}, \bar{2}) + \int d\bar{3}d\bar{4} w(\bar{1}, \bar{3}) \frac{\delta \langle \hat{\rho}(\bar{4}) \rangle}{\delta \varphi(\bar{3})} w(\bar{4}, \bar{2}). \quad (74)$$

If we split $\langle \hat{\rho} \rangle$ in an electronic and a nuclear part and use the chain rule we obtain

$$\begin{aligned} W(\bar{1}, \bar{2}) &= w(\bar{1}, \bar{2}) \\ &\quad + \int d\bar{3}d\bar{4}d\bar{5} w(\bar{1}, \bar{3}) \frac{\delta \langle \hat{n}(\bar{4}) \rangle}{\delta V(\bar{5})} \frac{\delta V(\bar{5})}{\delta \varphi(\bar{3})} w(\bar{4}, \bar{2}) \\ &\quad - \int d\bar{3}d\bar{4} w(\bar{1}, \bar{3}) \frac{\delta \langle \hat{N}(\bar{4}) \rangle}{\delta \varphi(\bar{3})} w(\bar{4}, \bar{2}) \\ &= w(\bar{1}, \bar{2}) + \int W(\bar{1}, \bar{5})P_e(\bar{4}, \bar{5})w(\bar{4}, \bar{2}) \\ &\quad - \int d\bar{3}d\bar{4} w(\bar{1}, \bar{3}) \frac{\delta \langle \hat{N}(\bar{4}) \rangle}{\delta \varphi(\bar{3})} w(\bar{4}, \bar{2}). \end{aligned} \quad (75)$$

This looks like the usual definition of the screened interaction except for a part induced by the nuclear charge density. We analyze this last term of the equation:

$$- \frac{\delta \langle \hat{N}(\bar{4}) \rangle}{\delta \varphi(\bar{3})} = i \langle T[\Delta \hat{N}_H(\bar{4}) \Delta \hat{\rho}_H(\bar{3})] \rangle, \quad (76)$$

where $\Delta \hat{A} = \hat{A} - \langle \hat{A} \rangle$ defines the fluctuation of an operator \hat{A} . If we split the total charge operator in its electronic and nuclear part we see that

$$\begin{aligned} - \frac{\delta \langle \hat{N}(\bar{4}) \rangle}{\delta \varphi(\bar{3})} &= -i \langle T[\Delta \hat{N}_H(\bar{4}) \Delta \hat{N}_H(\bar{3})] \rangle \\ &\quad + i \langle T[\Delta \hat{N}_H(\bar{4}) \Delta \hat{n}_H(\bar{3})] \rangle. \end{aligned} \quad (77)$$

The first term in the last equation represents the nuclear density-density correlation function

$$D(\bar{1}, \bar{2}) = -i \langle T[\Delta \hat{N}_H(\bar{1}) \Delta \hat{N}_H(\bar{2})] \rangle. \quad (78)$$

It is exactly this response function that interests us. It represents a correction to the electronic screened interaction due to nuclear density fluctuations. We will later see that for a solid its spectral function represents the lattice vibrations. We therefore want to include this function as a variable in the Hedin equations. This can be done with a method introduced by Baym.³⁸ We consider an extra term

$$\hat{H}_2 = - \int d\mathbf{R} \hat{N}(\mathbf{R})J(\mathbf{R}, t) \quad (79)$$

in the Hamiltonian that couples only to the nuclear density. We then see that

$$\frac{\delta \langle \hat{\rho}(\bar{1}) \rangle}{\delta J(\bar{2})} = i \langle T[\Delta \hat{N}_H(\bar{2}) \Delta \hat{\rho}_H(\bar{1})] \rangle = - \frac{\delta \langle \hat{N}(\bar{2}) \rangle}{\delta \varphi(\bar{1})}. \quad (80)$$

Furthermore we have

$$\begin{aligned} \frac{\delta\langle\hat{\rho}(\bar{1})\rangle}{\delta J(\bar{2})} &= -\frac{\delta\langle\hat{N}(\bar{1})\rangle}{\delta J(\bar{2})} + \frac{\delta\langle\hat{n}(\bar{1})\rangle}{\delta J(\bar{2})} = D(\bar{1},\bar{2}) \\ &+ \int d\bar{3} \frac{\delta\langle\hat{n}(\bar{1})\rangle}{\delta V(\bar{3})} \frac{\delta\langle V(\bar{3})\rangle}{\delta J(\bar{2})} = D(\bar{1},\bar{2}) \\ &+ \int d\bar{3}d\bar{4} P_e(\bar{1},\bar{3})w(\bar{3},\bar{4}) \frac{\delta\langle\hat{\rho}(4)\rangle}{\delta J(\bar{2})}. \end{aligned} \quad (81)$$

Solution of this integral equation yields

$$-\frac{\delta\langle\hat{N}(\bar{2})\rangle}{\delta\varphi(\bar{1})} = \frac{\delta\langle\hat{\rho}(\bar{1})\rangle}{\delta J(\bar{2})} = [(1 - P_e w)^{-1} D]_{\bar{1}\bar{2}}. \quad (82)$$

If we now insert this expression into Eq. (75) we find for W the integral equation

$$W = w + W P_e w + w(1 - P_e w)^{-1} D w. \quad (83)$$

If we solve this equation for W we find

$$W(\bar{1},\bar{2}) = W_e(\bar{1},\bar{2}) + \int d\bar{3}d\bar{4} W_e(\bar{1},\bar{3}) D(\bar{3},\bar{4}) W_e(\bar{4},\bar{2}), \quad (84)$$

where we defined the electronic part W_e of the screened interaction as

$$W_e = w(1 - P_e w)^{-1}. \quad (85)$$

This completes our derivation of the Hedin equations. Let us summarize our results in the following set of Hedin equations:

$$\Sigma(1,2) = i \int d3d4 G(1,3) W(\bar{1}^+, \bar{4}) \Gamma(3; 2, \bar{4}), \quad (86)$$

$$W(\bar{1},\bar{2}) = W_e(\bar{1},\bar{2}) + \int d\bar{3}d\bar{4} W_e(\bar{1},\bar{3}) D(\bar{3},\bar{4}) W_e(\bar{4},\bar{2}), \quad (87)$$

$$W_e = w(1 - P_e w)^{-1}, \quad (88)$$

$$P_e(\bar{1},\bar{2}) = -i \sum_{\sigma_1} \int d3d4 G(1,3) G(4,1) \Gamma(3; 4, \bar{2}), \quad (89)$$

$$\Gamma(1; 2; \bar{3}) = \delta(1-2) \delta(\bar{1}-\bar{3})$$

$$+ \int d4d5d6d7 \frac{\delta\Sigma(1,2)}{\delta G(4,5)} G(4,6) G(7,5) \Gamma(6; 7; \bar{3}). \quad (90)$$

If we put $D=0$ in these equations we obtain the usual Hedin equations of the rigid lattice and iteration of these equations leads to terms that are conveniently interpreted in terms of Feynman diagrams. As this is described clearly in the papers of Hedin and Lundqvist we will not carry out such an analysis here. The coupled equations derived here describe a general quantum system of electrons and nuclei and can therefore be used, as we will do below, to judge the range of validity of approximate Hamiltonians. To illustrate the gen-

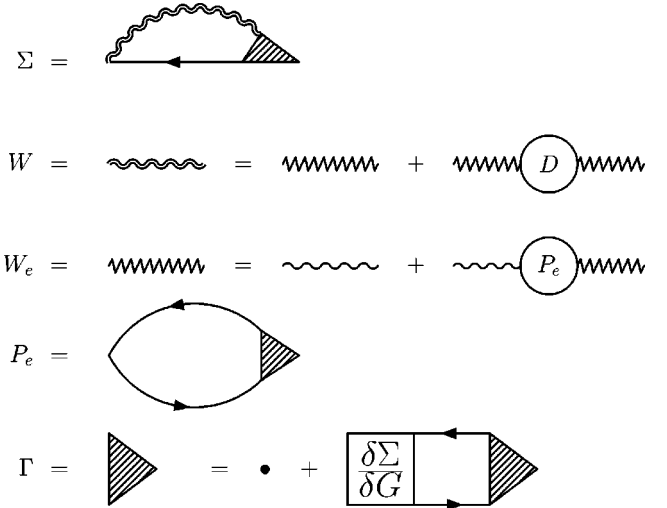


FIG. 1. Diagrammatic representation of the Hedin equations.

eral structure of these equations we have displayed them in Fig. 1. In this figure the interactions w , W_e , and W are represented by a wiggly, zigzag, and doubly wiggly line, respectively. The Green functions are represented with black lines with arrows and the bare vertex with a dot. Note that we do not have a determining equation for D itself. For this we would have to study the equation of motion of the nuclear creation and destruction operators which, however, leads to rather complicated expressions. The reason is that such an equation of motion will lead to taking commutators with the N_n -body operator $\hat{\Gamma}$. The appearance of such N_n -body terms is not surprising. After all, the commonly used Born-Oppenheimer potential of Eq. (10) is also a N_n -body quantity. These N_n -body terms make it difficult to find practical equations for the nuclear density-density correlation function D . However, in view of the quality of the Born-Oppenheimer phonons, we can expect that in practice we can get a good approximation for D from the Born-Oppenheimer wave functions. This approximation can then be inserted in the Hedin equations above and be iterated to obtain self-consistent approximations for the electronic Green function. The exact structure and the Born-Oppenheimer form of the nuclear density-density correlation function D will be studied in the following section.

V. THE PHONON-INDUCED INTERACTION BETWEEN THE ELECTRONS

In this section we will analyze the phonon-induced interaction between the electrons in more detail. Such an analysis provides us with more insight into the structure of the nuclear-nuclear correlation function and its possible approximations. It will also enable us to make a connection with the phenomenological Fröhlich Hamiltonian and to judge its validity.

In Eq. (84) of the preceding section we saw that we can write the screened interaction between the electrons as the sum of two terms,

$$W(\bar{1},\bar{2}) = W_e(\bar{1},\bar{2}) + W_{ph}(\bar{1},\bar{2}), \quad (91)$$

where we define

$$W_{ph}(\bar{1}, \bar{2}) = \int d\bar{3}d\bar{4} W_e(\bar{1}, \bar{3}) D(\bar{3}, \bar{4}) W_e(\bar{4}, \bar{2}). \quad (92)$$

The first term W_e in Eq. (91) represents a purely electronic screening. This is the only term when we restrict ourselves to the approximation of clamped nuclei. The second term W_{ph} describes an additional screening due to the motion of the nuclei and contains all the information on the electron-phonon interaction. The structure of this term becomes more transparent if we introduce the operator

$$\Delta \hat{V}_H(\mathbf{r}t) = - \int d\mathbf{R} \frac{\Delta \hat{N}_H(\mathbf{R}t)}{|\mathbf{r} - \mathbf{R}|} \quad (93)$$

and define the electronic dielectric function ϵ_e by

$$W_e(1,2) = \int d3 w(1,3) \epsilon_e^{-1}(2,3). \quad (94)$$

We can then write

$$W_{ph}(\bar{1}, \bar{2}) = \int d\bar{3}d\bar{4} \epsilon_e^{-1}(\bar{1}, \bar{3}) u(\bar{3}, \bar{4}) \epsilon_e^{-1}(\bar{4}, \bar{2}), \quad (95)$$

where

$$iu(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \langle T[\Delta \hat{V}_H(\mathbf{r}_1 t_1) \Delta \hat{V}_H(\mathbf{r}_2 t_2)] \rangle. \quad (96)$$

Inserting a complete set of eigenstates yields

$$iu(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \theta(t_1 - t_2) \sum_s e^{-i(t_1 - t_2)\Omega_s} F_s^*(\mathbf{r}_1) F_s(\mathbf{r}_2) + (1 \leftrightarrow 2), \quad (97)$$

where

$$F_s(\mathbf{r}) = \langle \Psi_s | \Delta \hat{V}(\mathbf{r}) | \Psi_0 \rangle, \quad (98)$$

and where Ψ_0 is the ground state with ground-state energy E_0 and Ψ_s an excited state of the system with energy E_s . We further defined $\Omega_s = E_s - E_0$ which represents an excitation energy. From this analysis we see that u only depends on time through the combination $t_1 - t_2$. This is simply a consequence of the time independence of the Hamiltonian and applies to all two-point quantities. We can therefore Fourier transform with respect to the relative time coordinate and write

$$W_{ph}(\mathbf{r}_1, \mathbf{r}_2, \omega) = \int d\mathbf{r}_3 d\mathbf{r}_4 \epsilon_e^{-1}(\mathbf{r}_1, \mathbf{r}_3, \omega) u(\mathbf{r}_3, \mathbf{r}_4, \omega) \times \epsilon_e^{-1}(\mathbf{r}_4, \mathbf{r}_2, \omega). \quad (99)$$

Using the relation

$$\theta(\tau) = \lim_{\eta \rightarrow 0^+} \frac{-1}{2\pi i} \int_{-\infty}^{+\infty} d\omega \frac{e^{-i\omega\tau}}{\omega + i\eta} \quad (100)$$

we can write

$$u(\mathbf{r}_1, \mathbf{r}_2, \omega) = \lim_{\eta \rightarrow 0^+} \sum_s \left(\frac{F_s^*(\mathbf{r}_1) F_s(\mathbf{r}_2)}{\omega - \Omega_s + i\eta} - \frac{F_s^*(\mathbf{r}_2) F_s(\mathbf{r}_1)}{\omega + \Omega_s - i\eta} \right). \quad (101)$$

In a system with time-reversal invariance we can always choose the eigenstates of the system real. We can therefore assume that the functions F_s are real. Then u simplifies to

$$u(\mathbf{r}_1, \mathbf{r}_2; \omega) = \lim_{\eta \rightarrow 0^+} \sum_s \frac{2\Omega_s F_s(\mathbf{r}_1) F_s(\mathbf{r}_2)}{\omega^2 - (\Omega_s - i\eta)^2}. \quad (102)$$

Using this expression we can write an expression of similar structure for W_{ph} :

$$W_{ph}(\mathbf{r}_1, \mathbf{r}_2; \omega) = \lim_{\eta \rightarrow 0^+} \sum_s \frac{2\Omega_s g_s(\mathbf{r}_1, \omega) g_s(\mathbf{r}_2, \omega)}{\omega^2 - (\Omega_s - i\eta)^2}, \quad (103)$$

where we defined

$$g_s(\mathbf{r}_1, \omega) = \int d\mathbf{r}_2 \epsilon_e^{-1}(\mathbf{r}_1, \mathbf{r}_2, \omega) F_s(\mathbf{r}_2). \quad (104)$$

Now the phonon-induced screened interaction is in a form suitable for analysis. Now we study the properties of the functions $F_s(\mathbf{r})$ and demonstrate that the energies Ω_s are of the order of phonon energies. The main observation is that the operator $\Delta \hat{V}(\mathbf{r})$ only consists of creation and annihilation operators involving nuclear coordinates. If we treat the states Ψ_0 and Ψ_s in the Born-Oppenheimer approximation it means that $\Delta \hat{V}$ connects only states that differ with respect to excitations in the nuclear part of the wave function. In the Born-Oppenheimer approximation these energies correspond to phonon excitation energies. Let us discuss this in more detail.

For $F_s(\mathbf{r})$ we have the expression

$$F_s(\mathbf{r}) = \int d\mathbf{R} \frac{\langle \Psi_s | \Delta \hat{N}(\mathbf{R}) | \Psi_0 \rangle}{|\mathbf{r} - \mathbf{R}|} = \sum_{j=1}^{N_n} Z_j \int dV \frac{\langle \Psi_s | \Delta \hat{\Gamma}(\mathbf{R}_1, \dots, \mathbf{R}_{N_n}) | \Psi_0 \rangle}{|\mathbf{r} - \mathbf{R}'_j|}, \quad (105)$$

where we used Eq. (45). For $s \neq 0$ this expression is nothing more than the matrix element $\langle \Psi_s | \hat{V}_n(\mathbf{r}) | \Psi_0 \rangle$ of the potential $\hat{V}_n(\mathbf{r})$ of Eq. (44). This function represents the Coulomb potential due to the nuclei felt by the electrons in the body-fixed frame. We know that for the ground state of the crystal this function is strongly peaked around equilibrium positions $\mathbf{R}_{i,0}$. This is a feature of the true ground state of the system and is independent of the BO approximation. For the functions $F_s(\mathbf{r})$ we can therefore do an expansion around the equilibrium positions and write (we suppress the arguments of $\Delta \hat{\Gamma}$)

$$\begin{aligned}
F_s(\mathbf{r}) &= \sum_{j=1}^{N_n} Z_j \int dV \frac{\langle \Psi_s | \Delta \hat{\Gamma} | \Psi_0 \rangle}{|\mathbf{r} - \mathbf{R}_{0,j}|} \\
&+ \sum_{j=1}^{N_n} Z_j \int dV \langle \Psi_s | \Delta \hat{\Gamma} | \Psi_0 \rangle \\
&\times (\mathbf{R}'_j - \mathbf{R}_{0,j}) \cdot \nabla_{\mathbf{R}_{0,j}} \frac{1}{|\mathbf{r} - \mathbf{R}_{0,j}|} + \dots \\
&= \sum_{j=1}^{N_n} \mathbf{u}_{j,s} \cdot \nabla_{\mathbf{R}_{0,j}} \frac{Z_j}{|\mathbf{r} - \mathbf{R}_{0,j}|} + \dots, \quad (106)
\end{aligned}$$

where we defined

$$\mathbf{u}_{j,s} = \int dV \langle \Psi_s | \Delta \hat{\Gamma} | \Psi_0 \rangle (\mathbf{R}'_j - \mathbf{R}_{0,j}) \quad (107)$$

and used that the integral over $\langle \Psi_s | \Delta \hat{\Gamma} | \Psi_0 \rangle$ vanishes. In a similar way we can in Eq. (106) also include terms from second order and higher in the deviations from equilibrium which will be necessary when we want to describe anharmonic effects. Until this point we did not need to use the Born-Oppenheimer equation. We only needed the property that the nuclear density is strongly peaked in the body-fixed frame. However, to calculate the expectation value of the nuclear displacement $\mathbf{u}_{j,s}$ in Eq. (107) we need approximate forms for the excited states Ψ_s . We will do this using the Born-Oppenheimer approximation. However, since Eq. (107) is expressed in coordinates with respect to the body-fixed frame [see Eq. (45)] we will have to transform the Born-Oppenheimer Hamiltonian of Eq. (10) to the body-fixed frame and expand in normal coordinates. How this is done is explained in detail in Appendix D. We can then use the Born-Oppenheimer approximation for the excited-state wave function in terms of normal coordinates \mathbf{Q} and write

$$\Psi_s = \Phi_e(\mathbf{r}, \mathbf{R}_0) \chi_s(\mathbf{Q}). \quad (108)$$

If there are N_n nuclei then there are $N = 3N_n - 6$ normal coordinates. The nuclear wave function is explicitly given in terms of these coordinates by

$$\chi_s = \xi_{i_1}(Q_1) \cdots \xi_{i_N}(Q_N) \quad (109)$$

and where the subindex i in Q_i is a multi-index $i = (\mathbf{q}, \lambda)$ for a normal coordinate characterized by wave vector \mathbf{q} and polarization direction λ . The indices i_1, \dots, i_N label the particular excited state χ_s , i.e., $\chi_s = |i_1 \cdots i_N\rangle$ and ξ_n is explicitly given by

$$\xi_n(Q_i) = H_n(Q_i) e^{-\Omega_i Q_i^2/2}, \quad (110)$$

where H_n is a Hermite polynomial. For the ground state we have $i_k = 0$. The electronic wave function Φ_e in Eq. (108) is the ground-state wave function of the clamped nuclei Hamiltonian of Eq. (8). Excited-state electronic wave functions need not be considered since they have no overlap with Ψ_0 in the matrix element of Eq. (107). To keep the presentation as simple as possible we will from now on only consider

monoatomic lattices with one nucleus with mass M and charge Z per unit cell. The normal coordinate is then defined by the relation^{4,19}

$$\mathbf{R}'_j - \mathbf{R}_{0,j} = \frac{1}{\sqrt{N_c M}} \sum_{\mathbf{q}, \lambda} Q_{\mathbf{q}, \lambda} \boldsymbol{\epsilon}_{\mathbf{q}, \lambda} e^{i\mathbf{q} \cdot \mathbf{R}_{0,j}}, \quad (111)$$

where N_c is the number of unit cells per unit volume and $\boldsymbol{\epsilon}_{\mathbf{q}, \lambda}$ is the polarization vector of the phonon. By inserting Eq. (111) into Eq. (107) we find that $\mathbf{u}_{j,s}$ is equal to

$$\mathbf{u}_{j,s} = \frac{1}{\sqrt{N_c M}} \sum_{\mathbf{q}', \lambda'} \boldsymbol{\epsilon}_{\mathbf{q}', \lambda'} e^{i\mathbf{q}' \cdot \mathbf{R}_{0,j}} \int dV \langle \Psi_s | \Delta \hat{\Gamma} | \Psi_0 \rangle Q_{\mathbf{q}', \lambda'}. \quad (112)$$

In Appendix D it is shown that

$$\int dV \langle \Psi_s | \Delta \hat{\Gamma} | \Psi_0 \rangle Q_i = \int d\mathbf{Q} \chi_s^*(\mathbf{Q}) Q_i \chi_0(\mathbf{Q}), \quad (113)$$

where we defined $d\mathbf{Q} = dQ_1 \cdots dQ_N$. The latter integral is readily evaluated to be

$$\begin{aligned}
\int d\mathbf{Q} \chi_s^*(\mathbf{Q}) Q_i \chi_0(\mathbf{Q}) &= \int dQ_i \xi_1(Q_i) Q_i \xi_0(Q_i) \\
&= (2\Omega_i)^{-1/2} \quad (114)
\end{aligned}$$

whenever $\chi_s = |0 \cdots 1 \cdots 0\rangle$ with 1 at position i and zero otherwise. We therefore only need to consider singly excited modes. If χ_s now corresponds to a state in which mode $\mathbf{q}\lambda$ is singly excited we obtain from Eqs. (112) and (114)

$$\mathbf{u}_{j, \mathbf{q}\lambda} = \frac{1}{\sqrt{2N_c M \Omega_{\mathbf{q}, \lambda}}} \boldsymbol{\epsilon}_{\mathbf{q}, \lambda} e^{i\mathbf{q} \cdot \mathbf{R}_{0,j}}. \quad (115)$$

Inserting this expression into Eq. (106) we finally obtain

$$W_{ph}(\mathbf{r}_1, \mathbf{r}_2, \omega) = \sum_{\mathbf{q}, \lambda} D_{\mathbf{q}\lambda}(\omega) g_{\mathbf{q}\lambda}(\mathbf{r}_1, \omega) g_{\mathbf{q}\lambda}^*(\mathbf{r}_2, \omega) \quad (116)$$

and where

$$D_{\mathbf{q}\lambda}(\omega) = \frac{2\Omega_{\mathbf{q}\lambda}}{\omega^2 - (\Omega_{\mathbf{q}\lambda} - i\eta)^2}. \quad (117)$$

We further defined

$$\begin{aligned}
g_{\mathbf{q}\lambda}(\mathbf{r}, \omega) &= (2MN_c \Omega_{\mathbf{q}\lambda})^{-1/2} \sum_i \int d\mathbf{r}_1 \epsilon_i^{-1}(\mathbf{r}, \mathbf{r}_1; \omega) \\
&\times \boldsymbol{\epsilon}_{\mathbf{q}, \lambda} \cdot \nabla_{\mathbf{r}_1} \frac{Z}{|\mathbf{r}_1 - \mathbf{R}_{0,i}|} e^{i\mathbf{q} \cdot \mathbf{R}_{0,i}}. \quad (118)
\end{aligned}$$

Expression (116) represents the effective interaction between the electrons that plays such an important role in the theory of superconductivity and has been derived before by Hedin and Lundqvist. However, their derivation is inconsistent since their final expression for the nuclear density-density correlation function has the periodic lattice symmetry

whereas their starting point is a completely rotationally and translationally invariant system. This inconsistency is repaired in the current derivation.

VI. COMPARISON TO THE FRÖHLICH HAMILTONIAN

Using the results of the preceding section we will now discuss the validity of the Fröhlich Hamiltonian. This Hamiltonian was developed by Fröhlich in the 1950s (Refs. 39–41) and has since then been widely used in different forms to describe phenomena that depend on the electron-phonon interaction.²⁰ We shall show here that the phenomenological Hamiltonian of Eq. (13) indeed leads to overscreening of phonon frequencies when higher-order terms are taken into account. To do this we will derive also some exact coupled equations for the Fröhlich Hamiltonian and compare them to the exact equations derived in the preceding sections. To make the discussion as simple as possible we again consider a monoatomic lattice of nuclei with mass M and charge Z . The Fröhlich Hamiltonian is then given by

$$\hat{H} = \hat{H}_{ph} + \hat{H}_e + \hat{H}_{e-ph}, \quad (119)$$

where the phonon Hamiltonian is given by

$$\hat{H}_{ph} = \sum_{\mu, \mathbf{q} \in \text{BZ}} \frac{1}{2} \hat{P}_{\mathbf{q}\mu}^\dagger \hat{P}_{\mathbf{q}\mu} + \frac{1}{2} \Omega_{\mathbf{q}\mu}^2 \hat{Q}_{\mathbf{q}\mu}^\dagger \hat{Q}_{\mathbf{q}\mu}, \quad (120)$$

where μ designates the polarization direction and the \mathbf{q} summation is restricted to the Brillouin zone denoted as BZ. The operators $\hat{P}_{\mathbf{q}\mu}$ and $\hat{Q}_{\mathbf{q}\mu}$ satisfy the usual canonical commutation relations as well as the relations $\hat{P}_{\mathbf{q}\mu}^\dagger = \hat{P}_{-\mathbf{q}\mu}$ and $\hat{Q}_{\mathbf{q}\mu}^\dagger = \hat{Q}_{-\mathbf{q}\mu}$. Here we used a notation close to that of Refs. 4 and 19. The electron-phonon interaction is given by

$$\hat{H}_{e-ph} = \sum_{\mu \mathbf{q}} \int d^3r \gamma_{\mathbf{q}\mu}(\mathbf{r}) \hat{n}(\mathbf{r}) \hat{Q}_{\mathbf{q}\mu}, \quad (121)$$

where the \mathbf{q} summation now extends over all wave vectors. In this expression the function $\gamma_{\mathbf{q}\mu}(\mathbf{r})$ is explicitly given by

$$\gamma_{\mathbf{q}\mu}(\mathbf{r}) = \frac{i}{V_0 \sqrt{MN_c}} e^{i\mathbf{q} \cdot \mathbf{r}} \tilde{v}_{e-n}(\mathbf{q}) \mathbf{q} \cdot \boldsymbol{\epsilon}_{\mathbf{q}\mu}, \quad (122)$$

where V_0 is the volume of the unit cell and $\tilde{v}_{e-n}(\mathbf{q})$ is the Fourier transform of the electron-nuclear interaction explicitly given by

$$\tilde{v}_{e-n}(\mathbf{q}) = -Z \int d^3r \frac{e^{-i\mathbf{q} \cdot \mathbf{r}}}{|\mathbf{r}|} = -\frac{4\pi Z}{|\mathbf{q}|^2}. \quad (123)$$

The function $\gamma_{\mathbf{q}\mu}$ further satisfies the useful relation $\gamma_{\mathbf{q}\mu}^* = \gamma_{-\mathbf{q}\mu}$. Note that we will follow Ref. 42 by denoting every Hamiltonian of the form in Eq. (119) as Fröhlich Hamiltonian, although often this term is reserved for special cases²⁰ of this expression. This nomenclature turned out to be most suitable for our general discussion. We now define a nuclear charge density operator by

$$\hat{N}(\mathbf{r}) = -\frac{\nabla^2}{4\pi} \left(\sum_{\mathbf{q}\mu} \gamma_{\mathbf{q}\mu}(\mathbf{r}) \hat{Q}_{\mathbf{q}\mu} \right). \quad (124)$$

In other words

$$\sum_{\mathbf{q}\mu} \gamma_{\mathbf{q}\mu}(\mathbf{r}) \hat{Q}_{\mathbf{q}\mu} = - \int d^3\mathbf{R} \frac{\hat{N}(\mathbf{R})}{|\mathbf{r}-\mathbf{R}|}. \quad (125)$$

We then define also $\hat{\rho}(\mathbf{r}) = \hat{n}(\mathbf{r}) - \hat{N}(\mathbf{r})$ as the operator for the total negative charge and we will introduce an external field $\varphi(\mathbf{r}t)$ coupling to this charge. In this way the full Hamiltonian is given by

$$\begin{aligned} \hat{H} = & \hat{H}_{ph} - \frac{1}{2} \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) \nabla^2 \hat{\psi}(\mathbf{x}) \\ & + \frac{1}{2} \int d\mathbf{x} d\mathbf{x}' \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}') \hat{\psi}(\mathbf{x}) w(\mathbf{r}, \mathbf{r}') \\ & - \int d^3r d^3\mathbf{R} \frac{\hat{n}(\mathbf{r}) \hat{N}(\mathbf{R})}{|\mathbf{r}-\mathbf{R}|} + \int d^3r \hat{\rho}(\mathbf{r}) \varphi(\mathbf{r}t). \end{aligned} \quad (126)$$

This Hamiltonian is, apart from the replacement of $\hat{T}_n + \hat{W}_{nn}$ by \hat{H}_{ph} and a different interpretation of the nuclear density, of identical form as the Hamiltonian of Eq. (49). The derivation of the Hedin equations using the functional derivative method therefore proceeds completely analogously as in Sec. IV and we obtain the identical Hedin equations (86)–(90), albeit with a different interpretation of the nuclear density-density correlation function D which is now evaluated with the density operator of Eq. (124) as

$$D(\bar{1}, \bar{2}) = -i \langle T[\Delta \hat{N}_H(\bar{1}) \Delta \hat{N}_H(\bar{2})] \rangle. \quad (127)$$

We further define the equivalent of operator $\Delta V_H(\mathbf{R}t)$ of Eq. (93) as

$$\Delta \hat{V}_H(\mathbf{r}t) = - \int d\mathbf{R} \frac{\Delta \hat{N}_H(\mathbf{R}t)}{|\mathbf{r}-\mathbf{R}|} = \sum_{\mathbf{q}\mu} \gamma_{\mathbf{q}\mu}(\mathbf{r}) \Delta \hat{Q}_{\mathbf{q}\mu, H}(t), \quad (128)$$

where we also defined the fluctuation operator $\Delta \hat{Q}_{\mathbf{q}\mu, H}(t) = \langle \hat{Q}_{\mathbf{q}\mu, H}(t) \rangle$. In analogy with the preceding section we now consider the time-ordered expectation value of this operator given by

$$\begin{aligned} iu(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = & \langle T[\Delta \hat{V}_H(\mathbf{r}_1 t_1) \Delta \hat{V}_H(\mathbf{r}_2 t_2)] \rangle \\ = & \sum_{\mathbf{q}\mathbf{q}', \mu\mu'} \gamma_{\mathbf{q}\mu}(\mathbf{r}_1) \\ & \times \langle T[\Delta \hat{Q}_{\mathbf{q}\mu}(t_1) \Delta \hat{Q}_{\mathbf{q}'\mu'}^\dagger(t_2)] \rangle \gamma_{\mathbf{q}'\mu'}^*(\mathbf{r}_2). \end{aligned} \quad (129)$$

We see that u and D can be calculated if we have an expression for the quantity

$$id_{\mathbf{q}\mathbf{q}'\mu\mu'}(t_1, t_2) = \langle T[\Delta \hat{Q}_{\mathbf{q}\mu}(t_1) \Delta \hat{Q}_{\mathbf{q}'\mu'}^\dagger(t_2)] \rangle \quad (130)$$

which we will refer to as the phonon propagator. We can derive an equation of motion for this quantity if we consider the equation of motion of $\hat{Q}_{\mathbf{q}\mu}(t)$. In order to do this we will also add an external field to the Hamiltonian of the form

$$\hat{H}_{ext}(t) = \sum_{\mu\mathbf{q}\in BZ} J_{\mathbf{q}\mu}(t)\hat{Q}_{\mathbf{q}\mu} + J_{\mathbf{q}\mu}^*(t)\hat{Q}_{\mathbf{q}\mu}^\dagger, \quad (131)$$

where $J_{\mathbf{q}\mu}^* = J_{-\mathbf{q}\mu}$ and where $J_{\mathbf{q}+\mathbf{G}\mu} = J_{\mathbf{q}\mu}$ with \mathbf{G} a reciprocal-lattice vector. We then have

$$\partial_t \hat{Q}_{\mathbf{q}\mu}(t) = -i[\hat{Q}_{\mathbf{q}\mu}(t), \hat{H}] = \hat{P}_{\mathbf{q}\mu}^\dagger(t). \quad (132)$$

The second derivative is then readily evaluated from the commutator with $\hat{P}_{\mathbf{q}\mu}^\dagger(t)$ to give

$$\begin{aligned} \partial_t^2 \hat{Q}_{\mathbf{q}\mu}(t) &= \partial_t \hat{P}_{\mathbf{q}\mu}^\dagger(t) = -\Omega_{\mathbf{q}\mu}^2 \hat{Q}_{\mathbf{q}\mu}(t) - \int d^3r \gamma_{\mathbf{q}\mu}^*(\mathbf{r}) \hat{n}_H(\mathbf{r}t) \\ &\quad - [J_{-\mathbf{q}\mu}(t) + J_{\mathbf{q}\mu}^*(t)]. \end{aligned} \quad (133)$$

If we take the functional derivative with respect to $J_{\mathbf{q}'\mu'}^*$ (where we treat J and J^* as independent) we obtain

$$\begin{aligned} (\partial_t^2 + \Omega_{\mathbf{q}\mu}^2) d_{\mathbf{q}\mathbf{q}'\mu\mu'}(t, t') &= -\delta(t-t') \bar{\delta}_{\mathbf{q}\mathbf{q}'} \delta_{\mu\mu'} \\ &\quad - \int d^3r \gamma_{\mathbf{q}\mu}^*(\mathbf{r}) \frac{\delta \langle \hat{n}_H(\mathbf{r}t) \rangle}{\delta J_{\mathbf{q}'\mu'}^*(t')}, \end{aligned} \quad (134)$$

where $\bar{\delta}_{\mathbf{q}\mathbf{q}'} = 1$ if \mathbf{q} and \mathbf{q}' differ by a reciprocal-lattice vector and zero otherwise. Since the density is given by the diagonal of the Green function we can write the latter equation as

$$\begin{aligned} (\partial_t^2 + \Omega_{\mathbf{q}\mu}^2) d_{\mathbf{q}\mathbf{q}'\mu\mu'}(t, t') &= -\delta(t-t') \bar{\delta}_{\mathbf{q}\mathbf{q}'} \delta_{\mu\mu'} - i \sum_{\sigma} \int d^3r d3 d4 \gamma_{\mathbf{q}\mu}^*(\mathbf{r}) \\ &\quad \times G(\mathbf{r}t\sigma, 3) G(4, \mathbf{r}t\sigma) \frac{\delta G^{-1}(3,4)}{\delta J_{\mathbf{q}'\mu'}^*(t')}. \end{aligned} \quad (135)$$

This equation can be rewritten as

$$\begin{aligned} (\partial_t^2 + \Omega_{\mathbf{q}\mu}^2) d_{\mathbf{q}\mathbf{q}'\mu\mu'}(t, t') &= -\delta(t-t') \bar{\delta}_{\mathbf{q}\mathbf{q}'} \delta_{\mu\mu'} + i \sum_{\mathbf{q}_1\alpha} \sum_{\sigma} \int d^3r dt_1 d3 d4 \gamma_{\mathbf{q}\mu}^*(\mathbf{r}) \\ &\quad \times G(\mathbf{r}t\sigma, 3) G(4, \mathbf{r}t\sigma) \bar{\Gamma}(34; \mathbf{q}_1\alpha t_1) d_{\mathbf{q}_1\mathbf{q}'\alpha\mu'}(t_1, t'), \end{aligned} \quad (136)$$

where we defined the vertex function as

$$\bar{\Gamma}(34; \mathbf{q}\alpha t) = -\frac{\delta G^{-1}(3,4)}{\delta \langle \hat{Q}_{\mathbf{q}\alpha}(t) \rangle}. \quad (137)$$

$$D = \bigcirc \cdots \bigcirc$$

$$d = \cdots = \text{---} + \text{---} \begin{array}{c} \curvearrowright \\ \curvearrowleft \end{array} \text{---}$$

$$\bar{\Gamma} = \triangleleft = \bullet + \begin{array}{|c|} \hline \frac{\delta \Sigma}{\delta G} \\ \hline \end{array} \triangleleft$$

FIG. 2. Diagrammatic representation of the self-consistent equations that determine the phonon propagator for the Fröhlich Hamiltonian.

This is a Dyson-like equation for the phonon propagator with the ‘‘bubble’’ $GG\bar{\Gamma}$. Now the electronic Green function satisfies

$$\begin{aligned} G^{-1}(1,2) &= G_0^{-1}(1,2) - \Sigma(1,2) - \delta(1-2) \\ &\quad \times \int d3 w(1,3) \langle \hat{\rho}(3) \rangle \\ &= G_0^{-1}(1,2) - \Sigma(1,2) - \delta(1-2) \\ &\quad \times \int d3 w(1,3) \langle \hat{n}(3) \rangle - \delta(1-2) \\ &\quad \times \sum_{\mathbf{q}\mu} \gamma_{\mathbf{q}\mu}(\mathbf{r}_1) \langle \hat{Q}_{\mathbf{q}\mu}(t_1) \rangle. \end{aligned} \quad (138)$$

Therefore

$$\begin{aligned} \bar{\Gamma}(12; \mathbf{q}\mu t) &= \delta(1-2) \delta(t_1-t) \gamma_{\mathbf{q}\mu}(\mathbf{r}_1) \\ &\quad + \int d4 d5 \frac{\delta \Sigma(1,2)}{\delta G(4,5)} \frac{\delta G(4,5)}{\delta \langle \hat{Q}_{\mathbf{q}\mu}(t) \rangle} \\ &= \delta(1-2) \delta(t_1-t) \gamma_{\mathbf{q}\mu}(\mathbf{r}_1) \\ &\quad + \int d4 d5 d6 d7 \frac{\delta \Sigma(1,2)}{\delta G(4,5)} G(4,6) G(7,5) \\ &\quad \times \bar{\Gamma}(67; \mathbf{q}\mu t), \end{aligned} \quad (139)$$

where it should be noted that we will also regard the phonon propagator d to be a functional of G .

Let us now discuss the results that we obtained. The central equations of this section are summarized diagrammatically in Fig. 2. The top line in this figure expresses the nuclear density-density correlation function in terms of the phonon propagator and is explicitly given by

$$D(\bar{1}, \bar{2}) = \sum_{\mathbf{q}\mathbf{q}'\mu\mu'} \alpha_{\mathbf{q}\mu}(\mathbf{r}_1) d_{\mathbf{q}\mathbf{q}'\mu\mu'}(t_1, t_2) \alpha_{\mathbf{q}'\mu'}^*(\mathbf{r}_2), \quad (140)$$

where we used Eqs. (127), (124), and (130) and we defined

$$\alpha_{\mathbf{q}\mu}(\mathbf{r}) = -\frac{\nabla^2}{4\pi} \gamma_{\mathbf{q}\mu}(\mathbf{r}). \quad (141)$$

In the figure the quantity $\alpha_{\mathbf{q}\mu}(\mathbf{r})$ is denoted by a small circle and the phonon propagator by a dotted line. In the second line of Fig. 2 we represent Eq. (136) in Dyson form where the dashed line represents the bare propagator d^0 that satisfies Eq. (144) and is discussed in more detail below. The last line of the figure represents Eq. (139) in which the bare vertex $\gamma_{\mathbf{q}\mu}$ is represented by a black dot. The equations represented in Figs. 1 and 2 completely determine all the properties of the Fröhlich Hamiltonian. Before discussing iterative solutions of these equations we first study the structure of the phonon propagator. The phonon propagator can be written in its Lehmann form as

$$id_{\mathbf{q}\mathbf{q}'\mu\mu'}(t_1, t_2) = \sum_s \theta(t_1 - t_2) e^{-i(t_1 - t_2)\Omega_s} \langle \Psi_0 | \Delta \hat{Q}_{\mathbf{q}\mu} | \Psi_s \rangle \\ \times \langle \Psi_s | \Delta \hat{Q}_{\mathbf{q}'\mu'}^\dagger | \Psi_0 \rangle + (1 \leftrightarrow 2). \quad (142)$$

If we take the phonon frequencies from a calculation of the Born-Oppenheimer surface and denote the corresponding propagator as d^0 we find using Eq. (114) that

$$id_{\mathbf{q}\mathbf{q}'\mu\mu'}^0(t_1, t_2) = \tilde{\delta}_{\mathbf{q}\mathbf{q}'} \delta_{\mu\mu'} \frac{1}{2\Omega_{\mathbf{q}\mu}} \theta(t_1 - t_2) e^{-i\Omega_{\mathbf{q}\mu}(t_1 - t_2)} \\ + (1 \leftrightarrow 2). \quad (143)$$

This propagator satisfies the equation of motion

$$(\partial_t^2 + \Omega_{\mathbf{q}\mu}^2) d_{\mathbf{q}\mathbf{q}'\mu\mu'}^0(t, t') = -\delta(t - t') \tilde{\delta}_{\mathbf{q}\mathbf{q}'} \delta_{\mu\mu'}. \quad (144)$$

If we Fourier transform with respect to $t_1 - t_2$ we obtain simply

$$d_{\mathbf{q}\mathbf{q}'\mu\mu'}^0(\omega) = \frac{\tilde{\delta}_{\mathbf{q}\mathbf{q}'} \delta_{\mu\mu'}}{\omega^2 - (\Omega_{\mathbf{q}\mu} - i\eta)^2}. \quad (145)$$

The function u is then given in frequency space by

$$iu(\mathbf{r}_1, \mathbf{r}_2, \omega) = \sum_{\mathbf{q}\mathbf{q}'\mu\mu'} \gamma_{\mathbf{q}\mu}(\mathbf{r}_1) \frac{\tilde{\delta}_{\mathbf{q}\mathbf{q}'} \delta_{\mu\mu'}}{\omega^2 - (\Omega_{\mathbf{q}\mu} - i\eta)^2} \gamma_{\mathbf{q}'\mu'}^*(\mathbf{r}_2) \\ = \sum_{\mu\mathbf{q} \in BZ} \frac{2\Omega_{\mathbf{q}\mu} F_{\mathbf{q}\mu}(\mathbf{r}_1) F_{\mathbf{q}\mu}^*(\mathbf{r}_2)}{\omega^2 - (\Omega_{\mathbf{q}\mu} - i\eta)^2}, \quad (146)$$

where

$$F_{\mathbf{q}\lambda}(\mathbf{r}) = (2\Omega_{\mathbf{q}\lambda})^{-1/2} \sum_{\mathbf{G}} \gamma_{\mathbf{q}+\mathbf{G},\lambda}(\mathbf{r}). \quad (147)$$

If we work out the latter term we have

$$F_{\mathbf{q}\lambda}(\mathbf{r}) = (2\Omega_{\mathbf{q}\lambda} M N_c)^{-1/2} \\ \times \frac{1}{V_0} \sum_{\mathbf{G}} \epsilon_{\mathbf{q}\lambda} \cdot \int d^3 r' e^{i(\mathbf{q}+\mathbf{G}) \cdot (\mathbf{r}-\mathbf{r}')} \nabla' \frac{Z}{|\mathbf{r}'|} \\ = (2\Omega_{\mathbf{q}\lambda} M N_c)^{-1/2} \epsilon_{\mathbf{q}\lambda} \cdot \sum_i \int d^3 r' e^{i\mathbf{q} \cdot (\mathbf{r}-\mathbf{r}')} \quad (148)$$

$$\times \delta(\mathbf{r}-\mathbf{r}'-\mathbf{R}_{0,i}) \nabla' \frac{Z}{|\mathbf{r}'|} \\ = (2\Omega_{\mathbf{q}\lambda} M N_c)^{-1/2} \sum_i e^{i\mathbf{q} \cdot \mathbf{R}_{0,i}} \epsilon_{\mathbf{q}\lambda} \cdot \nabla' \frac{Z}{|\mathbf{r}-\mathbf{R}_{0,i}|}, \quad (148)$$

where we used that $\epsilon_{\mathbf{q}} = \epsilon_{\mathbf{q}+\mathbf{G}}$. We see that with this approximation we obtain for the function $g_{\mathbf{q}\mu}$ an identical expression as in Eq. (118) of the preceding section.

Results will differ, however, as we sum the phonon propagator of the Fröhlich Hamiltonian to higher order. For instance, if we start iterating the coupled equations by taking for $\tilde{\Gamma}$ the first term on the right-hand side of Eq. (139) we obtain for the phonon propagator the equation

$$(\partial_t^2 + \Omega_{\mathbf{q}\mu}^2) d_{\mathbf{q}\mathbf{q}'\mu\mu'}(t, t') \\ = -\delta(t - t') \tilde{\delta}_{\mathbf{q}\mathbf{q}'} \delta_{\mu\mu'} + i \sum_{\mathbf{q}_1 \alpha} \sum_{\sigma} \int d^3 r d^3 \gamma_{\mathbf{q}\mu}^*(\mathbf{r}) \\ \times G(\mathbf{r}t\sigma, 3) G(3, \mathbf{r}t\sigma) \gamma_{\mathbf{q}_1 \alpha}(\mathbf{r}_3) d_{\mathbf{q}_1 \mathbf{q}', \alpha \mu'}(t_3, t'). \quad (149)$$

This equation gives d as a functional of G which can, using Eq. (140), subsequently be inserted into the Hedin equations of the Fröhlich Hamiltonian to obtain higher-order approximations for the self-energy Σ and thus a new $\tilde{\Gamma}$ from Eq. (139). The first iteration in Eq. (149) amounts to summing all diagrams for the phonon propagator that contain an electronic polarization bubble $P_e = -iGG$ which represents the electronic screening. By this dressing of the phonon propagator one obtains new screened phonon frequencies from its poles. However, since we know that the Born-Oppenheimer phonon frequencies are very close to realistic phonon frequencies, this leads to overscreening. This illustrates the double-counting problem discussed in the Introduction. We therefore obtain an important result. If we use Born-Oppenheimer phonon frequencies, then the exact coupled Hedin equations of Sec. IV and the Fröhlich Hamiltonian yield identical results *provided that we do not dress the phonon line in the Fröhlich model*. What does this imply for the results obtained with the Fröhlich Hamiltonian? First of all, many results obtained with this model were aimed at qualitative rather than quantitative agreement with experiment and often contain adjustable parameters that can be fitted to experimental data. On the other hand the calculations that used accurate frequencies and that aimed for quantitative agreement with experiment were often carried out in first-order perturbation theory in which double counting cannot occur. Nevertheless, it is important to be aware of the double-counting problem when one studies simple cases of the Fröhlich model that can be solved exactly.⁴³ The problem of double counting is, as explained, related to the fact that the phonon frequencies were determined in a way that already used the electronic part of the Hamiltonian. Indeed several works introduced bare phonon frequencies on the basis of a Hamiltonian as in Eq. (16) and one often considers

effective interactions between “ions” which are loosely defined as nuclei to which core electrons are rigidly attached. The disadvantage of the latter approach is that it is difficult to give it a rigorous basis since it involves the somewhat arbitrary definition of a core electron. Moreover the bare phonon frequencies one starts out with are very unphysical. One has to do an infinite summation to go from unrealistic ionic to more realistic dressed phonon frequencies. Apart from being a cumbersome procedure it is very unclear if the exact phonon frequencies (defined by the spectral function of the exact D) can even be obtained by such a procedure. Another disadvantage of the Fröhlich model as compared to the coupled equations of Sec. IV is that anharmonic effects in the electron-phonon coupling are absent. By using the coupled Hedin equations such effects can readily be included by expanding Eq. (106) to higher orders in $\mathbf{R}'_j - \mathbf{R}_{0,j}$. The general point we like to make is that in first-principles calculations the direct use of the coupled Hedin equations together with the BO approximation for the nuclear density-density correlation function presents a simple and general way of generating self-consistent approximations for electrons and phonons that are devoid from double-counting problems.

VII. PHONONS IN TIME-DEPENDENT DENSITY-FUNCTIONAL THEORY

Density-functional theory, as usually applied to electronic systems, expresses all observables as functionals of the electron density. In the case that we deal with the coupling between electronic and nuclear motion one needs an extension of electronic density-functional theory. Such an extension has been provided by the multicomponent density-functional approach of Kreibich and Gross^{23,44} and has been applied to diatomic molecules in strong laser fields. This theory has, however, not yet been investigated for the case of phonons. On the basis of the Hedin equations of Sec. IV one can, however, quite easily construct phonon corrections to results found with electronic density-functional theory. For instance, the electronic density-response function is readily calculated in time-dependent density-functional theory from^{9,10,45}

$$\chi(1,2) = \chi_0(1,2) + \int d3d4 \chi_0(1,3) \times [w(3,4) + f_{xc}(3,4)]\chi(4,2), \quad (150)$$

where χ_0 is the noninteracting density-response function of the Kohn-Sham system and f_{xc} is the so-called exchange-correlation kernel. From this function one can then readily construct $W_e = w\chi w$ and ϵ_e . Therefore by calculation of the phonon frequencies using the Born-Oppenheimer approximation, which can also be done within DFT,¹⁸ we can construct the effective interaction

$$W(1,2) = W_e(1,2) + W_{ph}(1,2) \quad (151)$$

from which the full dielectric function $\epsilon(1,2)$ can be obtained. This allows us then to calculate the phonon broadening of absorption spectra. The approach here is quite different from more *ad hoc* ways to calculate the electron-phonon

interaction within a DFT framework. Other works have done this by calculating the change in the effective Kohn-Sham potential v_s due to a shift of the nuclei.^{46–49} This amounts to using v_s rather than ϵ_e^{-1} in the expression for $W_{ph}(1,2)$. No justification for this procedure is given and from our results it appears that this procedure is indeed not justified and can only be regarded as an unfounded but simple approximation to ϵ_e^{-1} . The results, however, show that this approximation works quite well.

VIII. CONCLUSIONS

In this paper we have derived coupled equations for many-body Green functions, effective interactions, and vertices for the full system of electrons and nuclei. This approach was inspired by existing theoretical difficulties in standard derivations of the electron-phonon interaction. They involved (a) the breaking of the full rotational and translational symmetry of the original Hamiltonian and its corresponding neglect of rovibrational couplings and (b) the double-counting problem due to the use of Born-Oppenheimer phonon frequencies. The first problem was solved using a coordinate transformation that refers the electronic motion to a frame fixed to the nuclear framework. The second problem was solved by deriving coupled equations for observable quantities such as Green functions, rather than to try to define bare electrons and phonons and to expand parts of the Hamiltonian. We further showed a way to calculate the electron-phonon coupling within a density-functional framework and pointed out some problems in earlier work that calculates the electron-phonon coupling within a DFT context.

We hope that the work presented here will provide a useful basis for future first-principles approaches to the calculation of the electron-phonon interaction. Work on applications within a time-dependent density-functional context is in progress.

APPENDIX A: DEFINITIONS AND USEFUL RELATIONS

The Euler angles are specified by the fact that any rotation can be written as

$$\mathcal{R}(\alpha, \beta, \gamma) = \mathcal{R}_z(\gamma)\mathcal{R}_y(\alpha)\mathcal{R}_z(\beta), \quad (A1)$$

where \mathcal{R}_z and \mathcal{R}_y are rotations about the z and y axes. More details can be found in Refs. 29, 33, and 50. Let the column vectors of this rotation matrix be denoted \mathbf{e}_1 , \mathbf{e}_2 , \mathbf{e}_3 , i.e., $(\mathbf{e}_j)_i = \mathcal{R}_{ij}$. These vectors satisfy

$$\frac{\partial \mathbf{e}_i}{\partial \alpha} = \mathbf{e}_i \times \omega_\alpha, \quad (A2)$$

$$\frac{\partial \mathbf{e}_i}{\partial \beta} = \mathbf{e}_i \times \omega_\beta, \quad (A3)$$

$$\frac{\partial \mathbf{e}_i}{\partial \gamma} = \mathbf{e}_i \times \omega_\gamma, \quad (A4)$$

where we defined the following angular velocity vectors:

$$\omega_\alpha = \begin{pmatrix} \sin \gamma \\ \cos \gamma \\ 0 \end{pmatrix}, \quad \omega_\beta = \begin{pmatrix} -\sin \alpha \cos \gamma \\ \sin \alpha \sin \gamma \\ \cos \alpha \end{pmatrix}, \quad \omega_\gamma = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}. \quad (\text{A5})$$

Now all the angles depend on nuclear coordinates $\mathbf{R}_k = (R_x^k, R_y^k, R_z^k)$ where k labels the particle. Let us further introduce the short notation $\partial_i^k = \partial / \partial R_i^k$. Then from the equations above we find

$$\partial_i^k(\mathbf{e}_l)_j = \sum_{qr} \epsilon_{jqr}(\mathbf{e}_l)_q \Omega_{ri}^k, \quad (\text{A6})$$

where ϵ_{ijk} is the antisymmetric Levi-Civita tensor and where we defined

$$\Omega_{ri}^k = \omega_{\alpha,r} \partial_i^k \alpha + \omega_{\beta,r} \partial_i^k \beta + \omega_{\gamma,r} \partial_i^k \gamma \quad (\text{A7})$$

and where $\omega_{i,r}$ is the r th component of vector ω_i . Since the Euler angles are invariant under translation of all nuclear coordinates we can easily derive the useful condition

$$\sum_{k=1}^{N_n} \Omega_{ri}^k = 0. \quad (\text{A8})$$

If we now define

$$r_j'' = \sum_{jk} \mathcal{R}_{jl} r_l, \quad (\text{A9})$$

$$\mathbf{R}_j''' = \sum_{jk} \mathcal{R}_{jl} \mathbf{R}_l^n, \quad (\text{A10})$$

then we find the relations

$$\partial_i^k r_j'' = \sum_{qr} \epsilon_{jqr} r_q' \Omega_{ri}^k, \quad (\text{A11})$$

$$\partial_i^k \mathbf{R}_j''' = \mathcal{R}_{ji} \delta_{kn} + \sum_{qr} \epsilon_{jqr} R_q' \Omega_{ri}^k. \quad (\text{A12})$$

These relations will be useful in the following sections.

APPENDIX B: GENERAL FORM FOR THE CORIOLIS AND MASS-POLARIZATION TERMS

Here we will derive the general form of the mass-polarization and Coriolis terms presented in Sec. III. In that section we rotated the electronic coordinates to a frame that is attached to the nuclei but left the nuclear coordinates intact, i.e.,

$$\mathbf{r}'_i = \mathcal{R}(\alpha, \beta, \gamma)(\mathbf{r}_i - \mathbf{R}_{CMN}), \quad (\text{B1})$$

$$\mathbf{R}'_i = \mathbf{R}_i. \quad (\text{B2})$$

The wave function Ψ in the old coordinates is then related to wave function Φ in the new coordinates by

$$\Phi(\mathbf{r}'_1 \cdots \mathbf{r}'_{N_e}, \mathbf{R}'_1 \cdots \mathbf{R}'_{N_n}) = \Psi(\mathbf{r}_1 \cdots \mathbf{r}_{N_e}, \mathbf{R}_1 \cdots \mathbf{R}_{N_n}). \quad (\text{B3})$$

If we use

$$\partial_i^k r_j' = \sum_{qr} \epsilon_{jqr} r_q' \Omega_{ri}^k - \mathcal{R}_{ji} \frac{M_k}{M_{nuc}} \quad (\text{B4})$$

we obtain

$$\begin{aligned} \frac{\partial \Psi}{\partial \mathbf{R}_i^k} &= \frac{\partial \Phi}{\partial \mathbf{R}_i^k} + \sum_{l=1}^3 \sum_{n=1}^{N_e} \frac{\partial \Phi}{\partial r_l^{n'}} \frac{\partial r_l^{n'}}{\partial \mathbf{R}_i^k} = \frac{\partial \Phi}{\partial \mathbf{R}_i^k} - i \sum_r^3 \Omega_{ri}^k L_{e,r} \Phi \\ &\quad - i \frac{M_k}{M_{nuc}} \sum_l^3 \mathcal{R}_{li} P_{e,l} \Phi, \end{aligned} \quad (\text{B5})$$

where we used relation (B4) and where we defined the total electronic momentum and angular momentum operator

$$\mathbf{L}_e = \sum_{j=1}^{N_e} -i \mathbf{r}_j' \times \frac{\partial}{\partial \mathbf{r}_j'}, \quad (\text{B6})$$

$$\mathbf{P}_e = \sum_{j=1}^{N_e} -i \frac{\partial}{\partial \mathbf{r}_j'}. \quad (\text{B7})$$

The kinetic-energy operator therefore becomes

$$\begin{aligned} \hat{T}'_n &= - \sum_{k=1}^{N_n} \frac{1}{2M_k} \sum_i^3 \left(\partial_i^k - i \sum_r^3 \Omega_{ri}^k L_{e,r} \right. \\ &\quad \left. - i \frac{M_k}{M_{nuc}} \sum_l^3 \mathcal{R}_{li} P_{e,l} \right)^2. \end{aligned} \quad (\text{B8})$$

Let us work this term out. Because of the condition of Eq. (A8) there are no couplings between the \mathbf{L}_e and \mathbf{P}_e operators. We can then split the kinetic energy as

$$\hat{T}'_n = \hat{T}_n + \hat{T}_{MP} + \hat{T}_C, \quad (\text{B9})$$

where the mass-polarization terms are given by

$$\hat{T}_{MP} = \sum_{r=1}^3 (\mu_r^\dagger + \mu_r) P_{e,r} + \sum_{rs=1}^3 \beta_{rs} P_{e,r} P_{e,s}, \quad (\text{B10})$$

where

$$\mu_r = i \frac{1}{2M_{nuc}} \sum_{k=1}^{N_n} \sum_{i=1}^3 \mathcal{R}_{ri} \partial_i^k = - \frac{P'_{n,r}}{2M_{nuc}}, \quad (\text{B11})$$

$$\beta_{rs} = \frac{1}{2M_{nuc}^2} \sum_{k=1}^{N_n} M_k \sum_i^3 \mathcal{R}_{ri} \mathcal{R}_{si} = \frac{\delta_{rs}}{2M_{nuc}}, \quad (\text{B12})$$

where \mathbf{P}'_n is the nuclear momentum in the body-fixed frame. The Coriolis terms are given by

$$\hat{T}_C = \sum_{r=1}^3 (\nu_r^\dagger + \nu_r) L_{e,r} + \sum_{rs=1}^3 \alpha_{rs} L_{e,r} L_{e,s}, \quad (\text{B13})$$

where we defined

$$\nu_r = i \sum_{k=1}^{N_n} \frac{1}{2M_k} \sum_{i=1}^3 \Omega_{ri}^k \partial_i^k, \quad (\text{B14})$$

$$\alpha_{rs} = \sum_{k=1}^{N_n} \frac{1}{2M_k} \sum_{i=1}^3 \Omega_{ri}^k \Omega_{si}^k. \quad (\text{B15})$$

Our next task will be to provide more explicit expressions for ν_r and α_{rs} .

APPENDIX C: EXPLICIT FORM OF THE CORIOLIS TERM FOR SPECIFIC CHOICE OF THE BODY-FIXED FRAME

In this section we will demonstrate that for a large system the Coriolis terms become vanishingly small if we specify the Euler angles using the Eckart conditions given in Eq. (23). Since

$$0 = \sum_{i=1}^{N_n} M_i \mathbf{R}_{0,i} \times \mathcal{R}(\alpha, \beta, \gamma) \mathbf{R}_{CMN} \quad (\text{C1})$$

the Euler angles are equivalently defined by the conditions

$$0 = \sum_{i=1}^{N_n} M_i \mathbf{R}_{0,i} \times \mathcal{R}(\alpha, \beta, \gamma) \mathbf{R}_i. \quad (\text{C2})$$

This simply means that the angles are invariant under translations of the original coordinates. Classically the Eckart conditions enforce that in the rotated body-fixed frame the internal nuclear angular momentum with respect to the equilibrium configuration $\mathbf{R}_{i,0}$ is zero. This follows in a classical system directly from differentiation of the Eckart conditions with respect to time.²⁹ We now calculate the angular velocity vectors Ω_{ri}^k . An equation for these vectors can be obtained from a differentiation of the Eckart conditions with respect to \mathbf{R}_k . If we denote $\mathbf{R}_k'' = \mathcal{R} \mathbf{R}_k$ we obtain

$$\begin{aligned} 0 &= \partial_l^k \left(\sum_{njs} M_n \epsilon_{ijs} R_{0,j}^n R_s^{n''} \right) \\ &= \sum_{njs} M_n \epsilon_{ijs} R_{0,j}^n \left(\sum_{qr} \epsilon_{sqr} R_q^{n''} \Omega_{rl}^k + \mathcal{R}_{sl} \delta_{kn} \right) \\ &= \sum_{js} M_k \epsilon_{ijs} R_{0,j}^k \mathcal{R}_{sl} + \sum_{njr} M_n (\delta_{iq} \delta_{jr} - \delta_{ir} \delta_{jq}) R_{0,j}^n R_q^{n''} \Omega_{rl}^k \\ &= \sum_{js} M_k \epsilon_{ijs} R_{0,j}^k \mathcal{R}_{sl} + \sum_{nj} M_n (R_{0,j}^n R_i^{n''} \Omega_{jl}^k - R_{0,j}^n R_j^{n''} \Omega_{il}^k) \\ &= a_{li}^k - \sum_j J_{ij}(\mathbf{R}'') \Omega_{jl}^k, \end{aligned} \quad (\text{C3})$$

where the matrix $J(\mathbf{R})$ is defined as

$$J_{pq}(\mathbf{R}) = \sum_{k=1}^{N_n} M_k [(\mathbf{R}_{0,k} \cdot \mathbf{R}_k) \delta_{pq} - R_{0,p}^k R_q^k] \quad (\text{C4})$$

and where

$$a_{li}^k = \sum_{js} M_k \epsilon_{ijs} R_{0,j}^k \mathcal{R}_{sl} = M_k (\mathbf{R}_{0,k} \times \mathbf{e}_l)_i. \quad (\text{C5})$$

Note that the matrix J_{ij} is symmetric because of the Eckart conditions. Furthermore, the matrix $J(\mathbf{R}_0)$ is diagonal because of the conditions posed on the $\mathbf{R}_{0,i}$ and corresponds to the inertia tensor of the points $\mathbf{R}_{0,k}$. The angular momentum vectors Ω_{jl}^k can now be obtained from

$$\Omega_{jl}^k = \sum_p^3 (J^{-1})_{jp} a_{lp}^k. \quad (\text{C6})$$

Using the explicit form of a_{lp}^k and the fact that the $\mathbf{R}_{0,k}$ are defined in a frame with respect to the nuclear center of mass, we can check that condition (A8) is indeed satisfied. Let us now calculate the matrix α_{ij} of Appendix B. For this we need to evaluate

$$\sum_i \Omega_{vi}^k \Omega_{qi}^l = \sum_{st} (J^{-1})_{vs} (J^{-1})_{qt} \sum_i a_{is}^k a_{it}^l. \quad (\text{C7})$$

The last term in this equation is readily calculated to be

$$\begin{aligned} \sum_i a_{is}^k a_{it}^l &= \sum_{uvqr} \epsilon_{suv} \epsilon_{tqr} M_k M_l R_{0,u}^k R_{0,q}^l \sum_i \mathcal{R}_{vi} \mathcal{R}_{ri} \\ &= \sum_{uvq} \epsilon_{suv} \epsilon_{tqv} M_k M_l R_{0,u}^k R_{0,q}^l \\ &= \delta_{st} \left(\sum_q M_k M_l R_{0,q}^k R_{0,q}^l \right) - M_k M_l R_{0,t}^k R_{0,s}^l, \end{aligned} \quad (\text{C8})$$

where we used the orthogonality of the matrix \mathcal{R} . With this equation we obtain

$$\begin{aligned} \alpha_{vq} &= \sum_k \frac{1}{2M_k} \sum_i \Omega_{vi}^k \Omega_{qi}^k \\ &= \sum_{st} (J^{-1})_{vs} (J^{-1})_{qt} \sum_k \frac{1}{2M_k} \sum_i a_{is}^k a_{it}^k \\ &= \frac{1}{2} \sum_s (J^{-1})_{vs} I_{ss}(\mathbf{R}_0) (J^{-1})_{qs}, \end{aligned} \quad (\text{C9})$$

where $I_{ss}(\mathbf{R}_0)$ are the diagonal elements of the inertia tensor at the equilibrium positions \mathbf{R}_0 . Since this tensor is diagonal we can also write α_{vq} as a matrix product (where we keep in mind that J is a symmetric matrix and hence J^{-1} too):

$$\alpha_{pq} = \frac{1}{2} [J^{-1}(\mathbf{R}'') I(\mathbf{R}_0) J^{-1}(\mathbf{R}'')]_{pq}. \quad (\text{C10})$$

Since the matrix J is invariant under translations, i.e., $J(\mathbf{R} + \mathbf{a}) = J(\mathbf{R})$, we can rewrite this as

$$\alpha_{pq} = \frac{1}{2} [J^{-1}(\mathbf{R}') I(\mathbf{R}_0) J^{-1}(\mathbf{R}')]_{pq}, \quad (\text{C11})$$

where we translated over the vector $-\mathcal{R} \mathbf{R}_{CMN}$. It remains to calculate a more explicit form for the operator ν_r . For this term we find

$$\begin{aligned} \nu_r &= i \sum_{k=1}^{N_n} \frac{1}{2M_k} \sum_{i=1}^3 \Omega_{ri}^k \partial_i^k = i \sum_{k=1}^{N_n} \frac{1}{2M_k} \sum_{ip} (J^{-1})_{rp} a_{ip}^k \partial_i^k \\ &= \frac{i}{2} \sum_k \sum_{ipst} (J^{-1})_{rp} \epsilon_{pst} R_{0,s}^k \mathcal{R}_{ti} \partial_i^k = -\frac{1}{2} \sum_p (J^{-1})_{rp} L_{N,p}, \end{aligned} \quad (\text{C12})$$

where we defined the vibrational angular momentum of the nuclei by

$$\mathbf{L}_N = -i \sum_k \mathbf{R}_{0,k} \times \mathcal{R} \frac{\partial}{\partial \mathbf{R}_k}. \quad (\text{C13})$$

We see that if $\mathbf{R}' = \mathbf{R}_0$ then α_{pq} is diagonal and inversely proportional to the diagonal elements of the inertia tensor and also ν_r has the same proportionality. This is therefore a small quantity when the system is large. It is exactly this property that makes the Eckart conditions useful for the study of small molecular vibrations.

APPENDIX D: NORMAL COORDINATES IN THE BODY-FIXED FRAME

In this section we derive the body-fixed frame expression for the Born-Oppenheimer Hamiltonian that is used in Sec. V to construct the phonon propagator. Suppose we consider a nuclear Hamiltonian of the form

$$\hat{H} = -\sum_{k=1}^N \frac{1}{2M_k} \nabla_{\mathbf{R}_k}^2 + V(\mathbf{R}_1 \cdots \mathbf{R}_N). \quad (\text{D1})$$

In our case the potential V will describe the BO surface. We now consider the new coordinates

$$\mathbf{R}'_i = \mathcal{R}(\alpha, \beta, \gamma)(\mathbf{R}_i - \mathbf{R}_{CMN}), \quad (\text{D2})$$

where the Euler angles are determined by the Eckart conditions.

These \mathbf{R}'_i are shape coordinates in the sense that they are invariant under rotations and translations of the \mathbf{R}_i . They therefore span a $(3N-6)$ -dimensional space and are therefore dependent. If we remove \mathbf{R}'_N and \mathbf{R}'_{N-1} we are left with at most $3N-6$ independent shape coordinates. We therefore have to select six coordinates spanning the space ‘‘orthogonal’’ to the space of shape coordinates. One obvious candidate is the nuclear center of mass \mathbf{R}_{CMN} as defined in Eq. (18), which is not in the shape space since it is not translationally invariant. For the remaining coordinates we choose the Euler angles α, β, γ . These coordinates are translationally invariant but not rotationally invariant. We are therefore left with a choice of $3N-6$ shape coordinates. For this we take the general form

$$Q_i = \sum_{n=1}^N \sum_{j=1}^3 b_{ij}^n R_j^{n'}. \quad (\text{D3})$$

In order that the transformation from the old to the new coordinates be invertible the coefficients b_{ij}^k must be chosen in such a way that the new coordinates Q_i are orthogonal to the conditions

$$0 = \sum_k^N M_k \mathbf{R}'_k, \quad (\text{D4})$$

$$0 = \sum_k^N M_k \mathbf{R}_{0,k} \times \mathbf{R}'_k, \quad (\text{D5})$$

which are the center-of-mass fixing and Eckart conditions. For details on this procedure we refer to Refs. 34 and 51. We now have a new wave function Φ related to the old one Ψ by

$$\Phi(Q_1, \dots, Q_{3N-6}, \mathbf{R}_{CMN}, \alpha, \beta, \gamma) = \Psi(\mathbf{R}_1, \dots, \mathbf{R}_N). \quad (\text{D6})$$

Then partial differentiation yields

$$\begin{aligned} \frac{\partial \Psi}{\partial R_i^k} &= \frac{\partial \Phi}{\partial \alpha} \partial_i^k \alpha + \frac{\partial \Phi}{\partial \beta} \partial_i^k \beta + \frac{\partial \Phi}{\partial \gamma} \partial_i^k \gamma \\ &+ \sum_{l=1}^3 \frac{\partial \Phi}{\partial R_{CMN,l}} \partial_i^k R_{CMN,l} + \sum_{j=1}^{3N-6} \frac{\partial \Phi}{\partial Q_j} \partial_i^k Q_j, \end{aligned} \quad (\text{D7})$$

where the derivatives of the Euler angles can be expressed in terms of the coefficients Ω by inversion of Eq. (A7). This yields

$$\partial_i^k \alpha = \sin \gamma \Omega_{1i}^k + \cos \gamma \Omega_{2i}^k, \quad (\text{D8})$$

$$\partial_i^k \beta = -\frac{\cos \gamma}{\sin \alpha} \Omega_{1i}^k + \frac{\sin \gamma}{\sin \alpha} \Omega_{2i}^k, \quad (\text{D9})$$

$$\partial_i^k \gamma = \cot \alpha \cos \gamma \Omega_{1i}^k - \cot \alpha \sin \gamma \Omega_{2i}^k + \Omega_{3i}^k. \quad (\text{D10})$$

We then have

$$\frac{\partial \Phi}{\partial \alpha} \partial_i^k \alpha + \frac{\partial \Phi}{\partial \beta} \partial_i^k \beta + \frac{\partial \Phi}{\partial \gamma} \partial_i^k \gamma = -i \sum_{j=1}^3 \Omega_{ji}^k J_j \Phi, \quad (\text{D11})$$

where we defined the operators

$$iJ_1 = \sin \gamma \frac{\partial}{\partial \alpha} - \frac{\cos \gamma}{\sin \alpha} \frac{\partial}{\partial \beta} + \cot \alpha \cos \gamma \frac{\partial}{\partial \gamma}, \quad (\text{D12})$$

$$iJ_2 = \cos \gamma \frac{\partial}{\partial \alpha} + \frac{\sin \gamma}{\sin \alpha} \frac{\partial}{\partial \beta} - \cot \alpha \sin \gamma \frac{\partial}{\partial \gamma}, \quad (\text{D13})$$

$$iJ_3 = \frac{\partial}{\partial \gamma}, \quad (\text{D14})$$

which represent the rovibronic angular momentum operators relative to the body-fixed axes.³³ Using

$$\partial_i^k \mathbf{R}_l^{n'} = \sum_{qr} \epsilon_{lqr} \mathbf{R}_q^{n'} \Omega_{ri}^k + \mathcal{R}_{li} \left(\delta_{nk} - \frac{M_k}{M_{nuc}} \right) \quad (\text{D15})$$

we further obtain

$$\begin{aligned} \sum_{j=1}^{3N-6} \frac{\partial \Phi}{\partial Q_j} \partial_i^k Q_j = & -i \sum_r^3 L_{N,r} \Omega_{ri}^k \Phi + i \sum_r^3 \mathcal{R}_{ri} p_r^k \Phi \\ & - i \frac{M_k}{M_{nuc}} \sum_{r=1}^3 \sum_{m=1}^N \mathcal{R}_{ri} p_r^m \Phi, \end{aligned} \quad (\text{D16})$$

where we defined

$$p_r^m = -i \sum_{j=1}^{3N-6} b_{jr}^m \frac{\partial}{\partial Q_j}, \quad (\text{D17})$$

$$\mathbf{L}_N = -i \sum_m^N \mathbf{R}^{m'} \times \mathbf{p}^m. \quad (\text{D18})$$

Collecting our results together we obtain

$$\begin{aligned} \frac{\partial \Psi}{\partial \mathbf{R}_i^k} = & -i \sum_{r=1}^3 \Omega_{ri}^k (J_r + L_{N,r}) \Phi - i \sum_{r=1}^3 \mathcal{R}_{ri} p_r^k \Phi \\ & + \frac{M_k}{M_{nuc}} \left(\frac{\partial \Phi}{\partial R_{CMN,i}} - i \sum_{r=1}^3 \sum_{m=1}^N \mathcal{R}_{ri} p_r^m \Phi \right). \end{aligned} \quad (\text{D19})$$

The transformed kinetic energy is therefore given by

$$\begin{aligned} \hat{T}' = & - \sum_{k=1}^N \frac{1}{2M_k} \sum_{i=1}^3 \left[i \sum_{r=1}^3 \mathcal{R}_{ri} p_r^k - i \sum_{r=1}^3 \Omega_{ri}^k (J_r + L_{N,r}) \right. \\ & \left. + \frac{M_k}{M_{nuc}} \left(\frac{\partial}{\partial R_{CMN,i}} - i \sum_{r=1}^3 \sum_{m=1}^N \mathcal{R}_{ri} p_r^m \right) \right]^2. \end{aligned} \quad (\text{D20})$$

Let us work out this expression. Because of condition, Eq. (A8), there are no mixed expressions between the terms involving the angular momentum $J + L_N$ and the center-of-mass/polarization terms with prefactor M_k/M_{nuc} . We obtain

$$\hat{T}' = \hat{T}_{CMN} + \hat{T}_R + \hat{T}_{vib}, \quad (\text{D21})$$

where

$$\begin{aligned} \hat{T}_{CMN} = & - \frac{1}{2M_{nuc}} \nabla_{\mathbf{R}_{CMN}}^2, \\ \hat{T}_R = & \sum_{k=1}^N \sum_{irs}^3 \frac{1}{2M_k} \Omega_{ri}^k (J_r + L_{N,r}) \Omega_{si}^k (J_s + L_{N,s}) \\ & - \sum_{k=1}^N \frac{1}{2M_k} \sum_{irl=1}^3 \Omega_{ri}^k (J_r + L_{N,r}) \mathcal{R}_{li} p_l^k + \text{H.c.}, \\ \hat{T}_{vib} = & \sum_{k=1}^N \frac{1}{2M_k} \mathbf{p}^k \cdot \mathbf{p}^k - \frac{1}{2M_{nuc}} \sum_{k,n} \mathbf{p}^k \cdot \mathbf{p}^n. \end{aligned} \quad (\text{D22})$$

The term \hat{T}_{CMN} is simply the kinetic energy of the center of mass. The terms \hat{T}_R and \hat{T}_{vib} describe, loosely speaking, the rotational and vibrational part of the kinetic energy. If finally we choose the matrix b_{ij}^k in such a way that the vibrational kinetic energy becomes diagonal and that the potential V has a harmonic expansion in Q_i and neglect higher-order terms we obtain for $\hat{H}_{vib} = \hat{T}_{vib} + \hat{V}$ the form

$$\hat{H}_{vib} = \sum_{i=1}^{3N-6} \left(-\frac{1}{2} \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} \Omega_i^2 Q_i^2 \right), \quad (\text{D23})$$

where the Ω_i are identified with the vibrational phonon frequencies. The kinetic energy of the total nuclear center of mass can now be separated from the Hamiltonian. If we neglect Coriolis and mass-polarization terms and evaluate Ω_{ij}^k at the equilibrium positions \mathbf{R}_0^i then \hat{T}_R can be replaced by the rigid-rotor-type Hamiltonian

$$\hat{T}_R = \sum_{r,s}^3 \alpha_{rs} J_r J_s, \quad (\text{D24})$$

where α_{rs} is given by expression in Eq. (B15). Using the Eckart conditions we then find that α_{rs} is inversely proportional to the diagonal elements of the inertial tensor. We can now write the Hamiltonian as

$$\hat{H} = \hat{T}_{CMN} + \hat{T}_R + \hat{H}_{vib}. \quad (\text{D25})$$

The eigenfunctions of this Hamiltonian are of the form

$$\Phi_{\mathbf{q}ls} = \eta_{\mathbf{q}}(\mathbf{R}_{CMN}) \varphi_l(\alpha, \beta, \gamma) \chi_s(\mathbf{Q}), \quad (\text{D26})$$

where $\eta_{\mathbf{q}}$ is a plane wave corresponding to the center-of-mass motion

$$\eta_{\mathbf{q}}(\mathbf{R}_{CMN}) = \frac{1}{\sqrt{V}} e^{i\mathbf{q} \cdot \mathbf{R}_{CMN}}, \quad (\text{D27})$$

which is normalized in a volume V that will cancel out of our final equations. The function φ_l is an eigenfunction of the rigid-rotor Hamiltonian of Eq. (D24) and χ_s is an eigenfunction of the vibrational Hamiltonian \hat{H}_{vib} defined in Eq. (D23). We can now derive Eq. (113) for the transition matrix element. This matrix element is within the BO approximation given by

$$\Gamma_{i0} = \Psi_i^*(\mathbf{R}_1 \cdots \mathbf{R}_N) \Psi_0(\mathbf{R}_1 \cdots \mathbf{R}_N), \quad (\text{D28})$$

where i labels an excited state of the BO Hamiltonian. We note that $\Delta \Gamma_{i0} = \Gamma_{i0}$ for $i \neq 0$ and zero otherwise so that we only need to consider Γ_{i0} . Through Eq. (D6) we can express Γ_{i0} in coordinates in the body-fixed frame. Therefore

$$\int dV \Gamma_{i0} Q_j = \int dV \Phi_{\mathbf{q}ls}^* \Phi_0 Q_j. \quad (\text{D29})$$

The volume element dV has now to be expressed in body-fixed frame coordinates. This yields, considering a Jacobian consistent with the approximations made in the derivation of Eq. (D25), the result³²

$$dV = d\mathbf{R}_{CMN} \sin \alpha d\alpha d\beta d\gamma d\mathbf{Q}, \quad (\text{D30})$$

where $d\mathbf{Q} = dQ_1 \cdots dQ_{3N-6}$. The integral in Eq. (D29) is zero if \mathbf{q} and l are nonzero. The ground-state center-of-mass

and rigid-rotor wave functions can then be integrated out to yield

$$\int dV \Gamma_{i0} Q_j = \int d\mathbf{Q} \chi_s^*(\mathbf{Q}) \chi_0(\mathbf{Q}) Q_j \quad (\text{D31})$$

which proves Eq. (113).

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