Many-body Green’s function theory of electrons and nuclei beyond Born-Oppenheimer approximation

Ville J. Härkönen,1, Robert van Leeuwen,2 and Eberhard K. U. Gross1,3

1 Max Planck Institute of Microstructure Physics, Weinberg 2, D-06112 Halle, Germany
2 Department of Physics, Nanoscience Center, P.O. Box 33 FI-40014, University of Jyväskylä, Jyväskylä, Finland
3 Fritz Haber Center for Molecular Dynamics, Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

(Dated: June 18, 2019)

The method of many body Green’s functions is used to describe an arbitrary system of electrons and nuclei in a rigorous manner given the Hamiltonian of Coulombic interactions and kinetic energies. The theory given resolves the problem arising from the translational and rotational invariance of the Hamiltonian afflicting the existing theory based on the same technique. As a result, we derive a coupled set of exact equations for the electron and nuclei Green’s functions giving a systematic way to potentially compute various properties of a rather arbitrary many-body systems of electrons and nuclei beyond Born-Oppenheimer approximation, including molecules and solids. We discuss a special case of crystalline solids in more detail.

I. INTRODUCTION

The Born-Oppenheimer (BO) approximation is a rather central part in solving the many-body problem of electrons and nuclei in crystalline solids. This approximation has made the study of several physical properties computationally feasible and our current understanding about crystalline solids, for instance, is rather extensively based on it and its validity. In the BO approximation, the electron and nuclei problems are treated separately in a way that the nuclei coordinates are parameters in the electronic problem and the nuclei Hamiltonian contains no operators acting on electrons. Only the BO energy from the electronic problem enters the nuclei Hamiltonian. We can use various approaches, such as the density functional theory or the method of many-body Green’s functions, to solve the electronic problem alone. The nuclei part of the problem can be treated, for instance, by using the technique of many-body Green’s functions to describe various properties of crystals arising from nuclei. Usually the harmonic part of the nuclei Hamiltonian is diagonalized by a set of coordinate transformations and the phonon Green’s function theory is written in terms of the transformed coordinates. Therefore we have a closed form exact solution of the harmonic problem given the BO energy and the second order derivatives of it with respect to the nuclei coordinates. In addition to the electronic structure, the BO approximation has been successfully used to compute the phonon spectrum, thermal properties, and thermal conductivities of various materials in some cases reproducing the experimental results with reasonable accuracy. In some systems, however, the BO approximation may not be sufficiently accurate and more accurate methods are needed. The validity of the BO approximation is weaker for instance in some metals and materials such as graphene. Further, a theory beyond the BO approximation is needed in order to describe photo voltaics (solar cells, for example), chemical reactions and even vision, just to list a few examples. For more examples, see Ref. and references therein.

There are several first principle methods of going beyond the BO approximation. Among these are the wave function methods, multicomponent density functional theory, exact factorization, path integrals with Green’s functions and the Green’s function methods. In the Green’s function approach we start with a general many-body Hamiltonian (essentially comprising the Coulombic potentials and kinetic energies) and write the equations of motion (EOM) for the Green’s functions involved in order to formally obtain the general solution of the problem and then impose approximations. By starting with a generic Hamiltonian mentioned above, a general theory, in most cases, within the harmonic approximation to the nuclei, has been obtained for the electron and nuclei Green’s functions. In order to calculate desired observables within this theory, we may solve a coupled set of equations for the involved Green’s functions: Hedin’s equations for the electron Green’s function and related quantities and in a similar way the equations for the nuclei Green’s functions. In most cases, one has to impose further approximations in order to solve the equations for the Green’s functions involved, but in principle we have a general theory of many-body systems of electrons and nuclei, usually within the harmonic approximation.

There is, however, a known issue which prevents the use of the existing form of the exact theory to correctly describe solids and molecules, for example. As has been pointed out, the Hamiltonian used in the derivation is not suitable for the description as such. This issue arises from the translational and rotational invariance of the original Hamiltonian we start with and lead to a constant electron and nuclei densities in position space for the eigenstates of the Hamiltonian and spherically symmetric densities for the ground state with vanishing total angular momentum. In order to solve this issue, one can establish a set of coordinate transformations to...
obtain a Hamiltonian suitable for the description and this have already been done within the many-body Green’s function approach.\textsuperscript{50} However, no determining equation for the nuclei Green’s functions (or for the nuclei density-density correlation function) were given\textsuperscript{50} in order to find a coupled set of self-consistent equations for an arbitrary system of electrons and nuclei. Moreover, the earlier work was considering only crystalline solids excluding some terms important when the theory is imposed in the study of molecules, for example. The purpose of the present work is to derive such a set of equations with the general Hamiltonian without any approximations established. As a special case, we discuss what is the form of the theory when applied to crystalline solids and compare our results with those obtained earlier.

This paper is organized as follows. In Sec. II the transformed Hamiltonian suitable for the description of a system of electrons and nuclei is given. The EOM for the electrons are considered in Sec. III and for the nuclei Green’s functions in Sec. IV. The Hedin like equations for electrons are derived in Sec. V. We discuss how to determine some parameters related to the coordinate transformations in Sec. VII The general normal mode frequencies are derived in Sec. VIII and an expression for the nuclei self-energy (SE) due to the Coulombic interactions to the lowest order is given in Sec. VII B and is compared with the earlier results. The special case of crystalline solids is considered in Sec. VIII A. Phonons and their interactions are discussed in Sec. VIII B.

II. HAMILTONIAN

We denote the position coordinates of the system of \( N_e \) electrons and \( N_n \) nuclei in the laboratory frame as

\[
\mathbf{r}_i, \quad i = 1, \ldots, N_e, \quad \mathbf{R}_k, \quad k = 1, \ldots, N_n.
\]  

The Hamiltonian of this system in position representation can be written as

\[
H = T_n + T_e + V_{ee} + V_{en} + V_{nn},
\]  

where

\[
T_n = -\sum_{k=1}^{N_n} \frac{\hbar^2}{2M_k} \nabla^2 R_k, \quad T_e = \frac{\hbar^2}{2m_e} \sum_{i=1}^{N_e} \nabla^2 r_i,
\]

\[
V_{ee} = \sum_{i,i'=1}^{N_e} v(r_i, r_{i'}), \quad V_{en} = \sum_{i=1}^{N_e} \sum_{k=1}^{N_n} v(r_i, R_k),
\]

\[
V_{nn} = \sum_{k,k'=1}^{N_n} v(R_k, R_{k'}).
\]  

Here \( V_{ee}, V_{en} \) and \( V_{nn} \) are the Coulombic potentials such that

\[
v(r_i, R_k) = \frac{-Z_k \delta}{|r_i - R_k|}, \quad v(r_i, r_{i'}) = \frac{1}{2|r_i - r_{i'}|}, \quad v(R_k, R_{k'}) = \frac{Z_k Z_{k'} \zeta}{2 |R_k - R_{k'}|},
\]  

where \( \zeta = e^2/(4\pi\epsilon_0) \). The Hamiltonian \( H \) given by Eq. 2 is translationally and rotationally invariant and the one-body densities for the eigenstates of crystalline solids, we establish a coordinate transformation\textsuperscript{49,40,49,50,52} and write

\[
\mathbf{r}'' = \mathcal{R}(\mathbf{r}) = \mathcal{R}(\theta) (\mathbf{r}_i - \mathbf{R}_{cmn}), \quad i = 1, \ldots, N_e, \quad \mathbf{R}_k'' = \mathbf{R}_k - \mathbf{R}_{cmn}, \quad k = 1, \ldots, N_n - 1, \quad \mathbf{R}_{NN}'' = \mathbf{R}_{cmn},
\]  

where \( \mathcal{R} = \mathcal{R}(\theta) \) is the rotation matrix, \( \theta = (\theta_1, \theta_2, \theta_3) \) is the vector of Euler angles and Euler angles \( \theta_n \) are assumed to be functions of all the \( N_n - 1 \) nuclei variables denoted by \( \mathbf{R}'' \). Moreover, \( \mathbf{R}_{cmn} \) is the center-of-mass coordinate of the whole system of electrons and nuclei and \( \mathbf{R}_{cmn} \) is the nuclei center-of-mass given by

\[
\mathbf{R}_{cmn} = \frac{1}{M_{nuc}} \sum_{k=1}^{N_n} M_k \mathbf{R}_k, \quad M_{nuc} = \sum_{k=1}^{N_n} M_k.
\]  

We make the coordinate transformation in two stages, first we establish

\[
\mathbf{r}' = \mathbf{r}_i - \mathbf{R}_{cmn}, \quad i = 1, \ldots, N_e, \quad \mathbf{R}'_k = \mathbf{R}_k - \mathbf{R}_{cmn}, \quad k = 1, \ldots, N_n - 1, \quad \mathbf{R}'_{NN} = \mathbf{R}_{cmn},
\]  

and then the rotation of the electronic coordinates shown in Eq. 5. Such body-fixed frame transformations are used in the BO approximation as well when it is formulated for molecules\textsuperscript{1,53}. After transforming the Hamiltonian under the transformation given by Eq. 7 we have

\[
H = T_{tot} + V'_{ee} + V'_{en} + V'_{nn},
\]  

where \( V'_{ee}, V'_{en} \) and \( V'_{nn} \) are the Coulombic potentials written in terms of the primed variables and the kinetic energy \( T_{tot} = T_e + T_n \) is of the form

\[
T_{tot} = -\frac{\hbar^2}{2M} \nabla^2 \mathbf{r}_{cm} - \sum_{i=1}^{N_e} \frac{\hbar^2}{2m_i} \nabla^2 r_i - \sum_{k=1}^{N_n-1} \frac{\hbar^2}{2M_k} \nabla^2 R_k + \frac{\hbar^2}{2M_{nuc}} \sum_{i,i'=1}^{N_e} \nabla r_i' \cdot \nabla r_{i'} + \frac{\hbar^2}{2M_{nuc}} \sum_{k,k'=1}^{N_n} \nabla R_k \cdot \nabla R_{k'}.
\]
After establishing the second transformation \( r''_i = R(\theta) r'_i \) and \( R'_k = R'_k' \), we obtain

\[
H = T_{cm} + T'_e + T''_e + T''_{mp} + T''_{mpe} + T''_{cur} + T''_{cur}
+ V''_{ee} + V''_{en} + V''_{nn} + V_{ext},
\]

where \( V_{ext} \) is the external potential part added to the Hamiltonian (not originating from the coordinate transformation) and it is added in order to use the functional derivative techniques\(^{29, 49-51} \) in deriving the EOM. After the EOM are derived we put \( V_{ext} \) to zero. The transformed kinetic energies are

\[
T_{cm} = \frac{\hbar^2}{2M} \nabla^2 r'_{cm},
\]

\[
T'_e = \frac{\hbar^2}{2m_e} \sum_{i=1}^{N_e} \nabla^2 r''_i,
\]

\[
T''_e = -\sum_{k=1}^{N_a-1} \frac{\hbar^2}{2M_k} \nabla^2 R''_k,
\]

\[
T''_{mpe} = -\frac{\hbar^2}{2M_{nuc}} \sum_{i,j=1}^{N_e} \nabla r''_i \cdot \nabla r''_j,
\]

\[
T''_{mpe} = \frac{\hbar^2}{2M_{nuc}} \sum_{k,k'=1}^{N_a} \nabla R''_k \cdot \nabla R''_{k'},
\]

where the total mass is \( M = M_{nuc} + m_e N_e \) and the transformed Coulombic potentials are

\[
V''_{ee} = \sum_{i,j=1}^{N_e} u(r''_i, r''_j),
\]

\[
V''_{en} = \sum_{k,k'=1}^{N_a} \sum_{i=1}^{N_e} u(R''_k, R''_{k'}),
\]

\[
V''_{nn} = \sum_{k,k'=1}^{N_a} \sum_{i=1}^{N_a} u(r''_i, R''_{k'}),
\]

\[
R''_{N_a} = -\frac{1}{M_{nuc}} \sum_{k=1}^{N_a-1} M_k R''_k.
\]

Here, \( T_{cur} \) and \( T'_{cur} \) include the Coriolis and rotational-vibrational coupling terms and an explicit form of these quantities is given in Appendix [C](given in the abstract space). The center-of-mass kinetic energy \( T_{cm} \) commutes with all the other terms in the Hamiltonian and does not enter to the EOM and is neglected from now on. There are only \( N_a-1 \) primed nuclei coordinates appearing in the Hamiltonian. However, the number of degrees of freedom is still the same as before since one of the coordinates is the total center-of-mass coordinate of the system. The potential terms \( V''_{nn} \) and \( V''_{en} \) involving \( R''_{N_a} \) break the translational symmetry. The mass-polarization terms \( T''_{mp} \) and \( T''_{mpn} \) are expected to be rather small in the case of crystals and larger molecules since they are proportional to the inverse of the total nuclei mass. So far the Euler angles in Eq. [5] are assumed to be generic functions of the nuclei coordinates \( R''_k \) and we have not introduced any defining relations to them. There are many ways to choose these angles and here we assume that the Euler angles are defined through an implicit equation of the form

\[
F(\theta, R'') = 0.
\]

For example, one possible form of Eq. [13] is the Eckart condition and it can be written as

\[
\sum_{k=1}^{N_a-1} M_k x_k \times \nabla R''_k = 0.
\]

A relation connecting the quantities \( R''_k \) and \( x_k \) is given by Eq. [15]. The relations given by Eqs. [13] and [14] define the Euler angles and thus the rotation matrix as a function of the \( N_a-1 \) nuclei variables, \( R = R(\theta, R'') \). Some implicit conditions, like the Eckart condition, changes the permutation symmetry of the Hamiltonian\(^{49-51} \) with respect to our new nuclei variables leading to a more complicated commutators between the nuclei field operators of identical nuclei and therefore changes the symmetry of the wave functions written in terms of the transformed nuclei coordinates as well. However, the implicit condition does not change canonical commutation relations (Eq. [22]) between the nuclei position operators. This means that the EOM for the electron and nuclei Green’s functions remain the same whether or not the implicit condition changes the permutation symmetry of the Hamiltonian with respect to nuclei variables. In the case in which the implicit condition changes the aforementioned permutation symmetry and it turns out to be difficult to apply the theory because of the complicated symmetry, we may assume, as in the previous works\(^{8,48} \), that the nuclei are distinguishable. By doing so we avoid the problems potentially caused by a more complicated permutation symmetry. Some implicit conditions are not suitable for describing arbitrary systems, for example, in the case of linear molecules, the Eckart conditions as such are not well defined\(^{49, 47} \). Thus, despite our theory is in principle general, the choice of \( F(\theta, R'') \) in Eq. [13] may restrict the range of validity of the theory.

Next we establish yet another coordinate transformation of the nuclei coordinates and write the position coordinates as a sum of rest positions \( x_k \) (parameters) and displacements \( u_k \) (quantum variables), namely

\[
R''_k = x_k + u_k, \quad k = 1, \ldots, N_n - 1.
\]

We consider the determination of the rest positions \( x_k \) in more detail in Sec. [VI] and for now these are taken as arbitrary real parameters. Under this transformation, the position variables in the Hamiltonian \( H \) transform as Eq. [15] shows and in the kinetic energy terms (Eq. [11]), the derivatives included transform as \( \nabla R''_k \rightarrow \nabla u_k \). We have all the necessary steps made in order to write our Hamiltonian. We write the electronic parts of the Hamiltonian in the second quantization. This can be done in a
similar way as in the laboratory frame formulation since the transformed Hamiltonian has the same permutation symmetry with respect to the electronic variables as the original one. The nuclei part is written in the first quantization. After using Eq. [15], we write the Hamiltonian operator as (the center-of-mass kinetic energy neglected since it does not enter to the EOM)

$$\hat{H} = \hat{T}_{\text{tot}} + V_{\text{ee}} + \hat{V}_{\text{en}} + V_{\text{nn}} + \hat{V}_{\text{ext}},$$

where

$$\hat{T}_{\text{tot}} = \hat{T}_e' + \hat{T}_n' + \hat{T}_{mpe} + \hat{T}_{mpn} + \hat{T}_{cvr} + \hat{T}_{cvn}.'$$

Here $\hat{T}_{cvr}$ and $\hat{T}_{cvn}$ are given in Appendix D and the other kinetic energy terms are

$$\hat{T}_e' = \sum_{k=1}^{N_e-1} \frac{P_k \cdot \mathbf{P}_k}{2M_k},$$

$$\hat{T}_{mpe} = - \sum_{k,k'=1}^{N_e-1} \frac{P_k \cdot \mathbf{P}_{k'}}{2M_{\text{nuc}}},$$

$$\hat{T}_e = - \frac{\hbar^2}{2m_e} \int dr \hat{\psi}^\dagger(r) \nabla_r^2 \hat{\psi}(r),$$

$$\hat{V}_{mpn} = - \frac{\hbar^2}{2M_{\text{nuc}}} \int dr \int dr' \hat{\psi}^\dagger(r) \hat{\psi}(r') \nabla_r \cdot \nabla_r' \times \hat{\psi}(r') \hat{\psi}(r).$$

The potential energy terms in turn are

$$\hat{V}_{ee} = \frac{1}{2} \int dr \int dr' \varphi(r, r') \hat{\psi}^\dagger(r) \hat{\psi}(r') \hat{\psi}(r') \hat{\psi}(r),$$

$$\hat{V}_{en} = \int dr \int dr' \varphi(r, r') \hat{\psi}^\dagger(r) \hat{\psi}(r'),$$

$$\hat{V}_{nn} = \sum_{k,k'=1}^{N_e} \psi(x_k + \mathbf{u}_k, x_{k'} + \mathbf{u}_{k'}).$$

and

$$\hat{V}_{ext} = \int dr \varphi(rt) \hat{\psi}^\dagger(r) + \int dr \varphi(rt) \hat{\psi}(r)$$

$$\quad + \sum_p \int dr U_p(rt) \hat{\psi}^\dagger(r) + \sum_{k=1}^{N_e-1} \mathbf{J}(kt) \cdot \mathbf{u}_k$$

$$\quad + \int dr \varphi(rt) \hat{\psi}(r),$$

where we use $\hat{\psi}(r) = \hat{\psi}^\dagger(r) \hat{\psi}(r)$. In these equations $\varphi(r, r') = \zeta/|r - r'|$ and

$$\hat{n}_e(r) = - \sum_{k=1}^{N_e} \int d\mathbf{R}_k \delta(r - \mathbf{R}_k) \hat{R}_k'',$$

$$\hat{V}_{en}(r) = \sum_{k=1}^{N_e-1} \int d\mathbf{R}_k \frac{-Z_k \zeta}{|r - \mathbf{R}_k|} \hat{R}_k''.$$

The operators $\hat{u}_\alpha(k), \hat{p}_{\alpha'}(k'), \hat{\psi}^\dagger(r)$ and $\hat{\psi}(r)$ satisfy the following commutation and anti-commutation relations

$$[\hat{u}_\alpha(k), \hat{p}_{\alpha'}(k')]_+ = i\hbar \delta_{\alpha\alpha'} \delta_{kk'},$$

$$[\hat{\psi}(r), \hat{\psi}^\dagger(r')]_+ = \delta(r - r').$$

When necessary (see Sec. VIII), we use the notation $k = ik$ and so on, which is perhaps more suitable in the case of crystalline solids, see Appendix A for the description of this notation. In the case of solids, we also impose the periodic boundary conditions. So far we have not established any approximations. We have now set up the Hamiltonian to work with and derive the EOM for the electron and nuclei Green’s functions by using it in Secs. III and IV.

III. EQUATIONS OF MOTION FOR ELECTRONS

Here we derive the EOM for the electron Green’s function. We denote an ensemble average for an operator $\hat{\theta}(t)$ (in the Heisenberg picture) as

$$\langle \hat{\theta}(t) \rangle = \frac{1}{\langle \hat{\rho} \rangle} \sum_n \langle \phi_n | \hat{\rho} \hat{\theta}(t) | \phi_n \rangle = \text{Tr} \left[ \hat{\rho} \hat{\theta}(t) \right],$$

where $\{ | \phi_n \rangle \}$ is a set of orthonormal basis kets. The density operator is of the form

$$\hat{\rho} = e^{-\beta \hat{H}^M} Z^{-1},$$

where

$$\hat{H}^M = \hat{H} - \mu_e \hat{N}_e, \quad \hat{N}_e = \int dr \hat{n}_e(r),$$

and $\mu_e$ is the chemical potential of the electrons. Thus, the density operator in Eq. (24) is chosen to describe systems with a fixed number of nucleii. Here the notation is such that the time variable $t$ could be taken as a real variable or variable on the Keldysh contour. This is justifiable since in both cases the EOM are the same. If the time variables are taken to be variables in the Keldysh contour, the time integrals are taken to be integrals on the contour, see Ref. 13 for details.

We start by writing the EOM for the field operator $\hat{\psi}(rt)$ (operator in the Heisenberg picture), namely

$$i\hbar \frac{\partial}{\partial t} \hat{\psi}(rt) = \hat{D}(rt) \hat{\psi}(rt)$$

$$+ \int dr' \varphi(r, r') \hat{\psi}^\dagger(r') \hat{\psi}(r') \hat{\psi}(rt)$$

$$- \frac{\hbar^2}{M_{\text{nuc}}} \int dr' \hat{\psi}^\dagger(r') \nabla_r \cdot \nabla_r' \hat{\psi}(r') \hat{\psi}(rt)$$

$$+ 2 \sum_{\beta, \sigma, \gamma, \gamma'} \hat{L}^{(3)}_{\beta \gamma \gamma'} \int dr' \hat{\psi}^\dagger(r') \hat{\psi}(r') \frac{\partial^2}{\partial r_\beta \partial r_\gamma} \hat{\psi}(r') \hat{\psi}(rt),$$

where $\hat{L}^{(3)}_{\beta \gamma \gamma'} = \frac{i}{4} \epsilon_{\beta \gamma \gamma'} \int d\mathbf{r} \varphi(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}(\mathbf{r}) \hat{\psi}(rt).$
where
\[
\hat{D}(rt) = -\frac{\hbar^2}{2m} \nabla^2 r + U(rt) + \varphi(rt)
+ \int dr' v(r, r') \hat{n}_n(r') + \sum_{\beta, \gamma} \hat{L}^{(1)}_{\beta \gamma}(ri) \frac{\partial}{\partial r_\beta},
\]
\[
+ \sum_{k=1}^{N_r-1} \sum_{\alpha, \beta, \gamma} \hat{L}^{(2)}_{\alpha \beta \gamma}(k) \hat{p}_n(k) r_\gamma \frac{\partial}{\partial r_\beta},
\]
\[= \sum_{\beta, \gamma} \hat{L}^{(1)}_{\beta \gamma}(ri) \frac{\partial}{\partial r_\beta},
\]
and
\[
\hat{L}^{(1)}_{\beta \gamma}(ri) = \hat{T}^{(1)}_{\beta \gamma}(ri) + \hat{M}^{(1)}_{\beta \gamma}(
\hat{L}^{(2)}_{\alpha \beta \gamma}(k) = \hat{T}^{(2)}_{\alpha \beta \gamma}(k) + \hat{M}^{(2)}_{\alpha \beta \gamma}(k),
\hat{L}^{(3)}_{\gamma \sigma \gamma' \beta} = \hat{M}^{(3)}_{\gamma \sigma \gamma' \beta} + \hat{T}^{(3)}_{\gamma \sigma \gamma' \beta}.\]

The quantities in Eq. 28 originate from the Coriolis and vibrational-rotational coupling terms, see Appendix C. Define the electron Green's function as 7,10,13
\[
G(rt, rt') \equiv -\frac{i}{\hbar} \text{Tr} \left[ \frac{e^{-\beta H_M} T \left\{ \hat{\psi}(rt) \hat{\psi}^\dagger(rtt') \right\}}{e^{-\beta H_M}} \right],
\]
where
\[
\left\langle T \left\{ \hat{\psi}(rt) \hat{\psi}^\dagger(rtt') \right\} \right\rangle = \theta(t - t') \left\langle \hat{\psi}(rt) \hat{\psi}^\dagger(rtt') \right\rangle
+ \theta(t' - t) \left\langle \hat{\psi}(r'tt) \hat{\psi}^\dagger(rt) \right\rangle,
\]
and \(G(rt, rtt')\) satisfies the Kubo-Martin-Schwinger boundary conditions.7,13 The EOM for the Green's function reads
\[
i\hbar \frac{\partial}{\partial t} G(rt, rtt') = \left\{ 0 \right\} + \delta(t - t') \delta(r - r').
\]
After using Eq. 28 we find that
\[
\left[ i\hbar \frac{\partial}{\partial t} \right] G(rt, rtt') = \delta(t - t') \delta(r - r') + S(rt, rtt') + S'(rt, rtt'),
\]
where the total density is defined by \(\hat{n}(r) \equiv \hat{n}_e(r) + \hat{n}_n(rtt')\) and
\[
S'(rt, rtt') = \frac{1}{\hbar} \int dr'' v(r, r'') \times \left\langle T \left\{ \hat{n}(r''t) \hat{\psi}(rt) \hat{\psi}^\dagger(rtt') \right\} \right\rangle,
\]
\[
D(rt) \equiv -\frac{\hbar^2}{2m_e} \nabla^2 r + U(rt) + \varphi(rt).
\]
By substracting the quantity (we use the shorthand notation given by Eq. A3 of Appendix A)
\[
\int d3v(1, 3) \left\langle \hat{n}(3) \right\rangle G(1, 2),
\]
from both sides of Eq. 28 we find that
\[
\left[ i\hbar \frac{\partial}{\partial t_1} + \frac{\hbar^2}{2m_e} \nabla^2 r_1 - V_{tot}(1) \right] G(1, 2) = \delta(1 - 2) + S(1, 2) + \tilde{S}(1, 2),
\]
where
\[
\tilde{S}(1, 2) \equiv S'(1, 2) - \int d3v(1, 3) \left\langle \hat{n}(3) \right\rangle G(1, 2),
\]
\[V_{tot}(1) \equiv \varphi(1) + U(1) + \int d3v(1, 3) \left\langle \hat{n}(3) \right\rangle .\]
body-fixed frame in contrast to the laboratory frame formulation\cite{10,15} and the SE also contains the contributions from the kinetic energy terms neglected in the earlier body-fixed frame formulation\cite{20}. By neglecting the kinetic energy terms \( \hat{T}_{\text{cvar}} \) and \( \hat{T}'_{\text{cvar}} \) in the first place leads to Eqs. \( 41 \) and \( 42 \) with \( \Sigma_c (1,3) = 0 \) for \( c = 1, 2, 3 \) and thus \( \Sigma (1,3) = \Sigma (1,3) \). In this case, we obtain similar equations as in the earlier work on the body-fixed frame\cite{20}. Thus all the rather complicated kinetic energy terms appearing in the theory, originating from the body-fixed frame transformation, are hidden in the SE’s \( \Sigma_c (1,3) \). We give an explicit and approximative form of \( \Sigma_c (1,3) \) in Eqs. \( 94 \) and \( 95 \) of Sec. \( V \) Here we obtained the necessary EOM for electrons and we further write the Hedin like equations for electrons in Sec. \( V \) which may be in some cases useful in deriving expressions for the SE originating from the Coulombic interaction, \( \Sigma (1,2) \).

IV. EQUATIONS OF MOTION FOR NUCLEI

Next we set out to derive the EOM for nuclei. The connection of the nuclei and electron equations is discussed in more detail in Sec. \( V \) where we give some justification for the choice of quantities for which the nuclei EOM are written. We start by writing the Heisenberg EOM for the displacements, namely

\[
i\hbar \frac{\partial}{\partial t} \hat{u}_\alpha (kt) = \left[ \hat{u}_\alpha (kt), \hat{H} (t) \right]_-,\quad (44)
\]

After computing the commutators by using Eq. \( 10 \) [see also Eq. \( 28 \)]

\[
M_k \frac{\partial}{\partial t} \hat{u}_\alpha (kt) = \hat{p}_\alpha (kt) - \frac{M_k}{M_{\text{nuc}}} \sum_{k' = 1}^{N_u - 1} \hat{p}_\alpha (k'' t)
+ M_k \sum_{\beta, \gamma} \int d\mathbf{r}_\gamma \frac{\partial}{\partial r_\beta} \hat{L}^{(2)}_{\alpha \beta \gamma} (k) \hat{n}_\gamma (r_\beta).
\]

(45)

After differentiating Eq. \( 45 \) with respect to time and taking an ensemble average

\[
M_k \frac{\partial^2}{\partial t^2} \langle \hat{u}_\alpha (kt) \rangle = K_\alpha (kt) + \sum_{c = 1}^{4} K^{(c)}_\alpha (kt) - J_\alpha (kt),
\]

(46)

where (we use \( \hat{T}''_{\text{cvar}} = \hat{T}_{\text{cvar}} + \hat{T}''_{\text{cvar}} \))

\[
K_\alpha (kt) \equiv \frac{1}{\iota \hbar} \left\langle \hat{p}_\alpha (kt) \hat{V}_{\text{en}}'' + \hat{V}_{\text{en}}'' \right\rangle + \cdots,
\]

\[
K^{(1)}_\alpha (kt) \equiv \frac{i M_k}{\hbar M_{\text{nuc}}} \sum_{k' = 1}^{N_u - 1} \left\langle \hat{p}_\alpha (k' t) \hat{V}_{\text{en}}'' + \hat{V}_{\text{en}}'' \right\rangle.
\]

\[
K^{(2)}_\alpha (kt) \equiv \frac{1}{\iota \hbar} \left\langle \hat{p}_\alpha (kt) \hat{V}_{\text{cvar}}'' \right\rangle .
\]

\[
K^{(3)}_\alpha (kt) \equiv \frac{i M_k}{\hbar M_{\text{nuc}}} \sum_{k' = 1}^{N_u - 1} \left\langle \hat{p}_\alpha (k' t) \hat{V}_{\text{cvar}}'' \right\rangle.
\]

\[
K^{(4)}_\alpha (kt) \equiv \frac{1}{\iota \hbar} \sum_{\beta, \gamma} \int d\mathbf{r}_\gamma \frac{\partial}{\partial r_\beta} \times \left\langle \hat{L}^{(2)}_{\alpha \beta \gamma} (k) \hat{n}_\gamma (r_\beta), \hat{H} (t) \right\rangle .
\]

(47)

In the first two quantities of Eq. \( 44 \) all the other terms except those originating from the external potentials are explicitly shown.

In order to obtain the EOM for the nuclei Green’s function we take a functional derivative of Eq. \( 45 \) with respect to \( J_\beta (k' t) \) and write

\[
M_k \frac{\partial^2}{\partial t^2} D_{\alpha \beta} (kt, k' t') = -\delta_{\alpha \beta} \delta_{k k'} \delta (t - t') + K_{\alpha \beta} (kt, k' t')
+ \sum_{c = 1}^{4} K^{(c)}_{\alpha \beta} (kt, k' t'),
\]

(48)

where

\[
\delta \langle \hat{u}_\alpha (kt) \rangle = \frac{1}{i \hbar} \langle \hat{T} \{ \hat{u}_\alpha (kt), \hat{u}_\beta (k' t') \} \rangle
- \frac{1}{i \hbar} \langle \hat{u}_\alpha (kt) \rangle \langle \hat{u}_\beta (k' t') \rangle
= D_{\alpha \beta} (kt, k' t'),
\]

\[
K_{\alpha \beta} (kt, k' t') \equiv \frac{\delta K_{\alpha} (kt)}{\delta J_\beta (k' t')}.
\]

\[
K^{(c)}_{\alpha \beta} (kt, k' t') \equiv \frac{\delta K^{(c)}_{\alpha} (kt)}{\delta J_\beta (k' t')}.
\]

(49)

We write yet another form of Eq. \( 48 \) by assuming that \( D_{\alpha \beta} (kt, k' t') \) is invertible, namely, Eq. \( 48 \) can be written in terms of the nuclei SE’s

\[
\Pi_{\alpha \alpha'} (kt, k' t) \equiv - \sum_{k' , \delta} \int dt' K_{\alpha \beta} (kt, k' t') D^{-1}_{\beta \alpha} (k' t', k' t),
\]

\[
\Pi^{(c)}_{\alpha \alpha'} (kt, k' t) \equiv - \sum_{k' , \delta} \int dt' K^{(c)}_{\alpha \beta} (kt, k' t') D^{-1}_{\beta \alpha} (k' t', k' t),
\]

(50)
as
\[
M_k \frac{\partial^2}{\partial t^2} D_{\alpha\beta}(kt, k't') = -\sum_{k''\cdot\alpha'} \int dt'' \Pi_{\alpha\alpha'}(kt, k''t'') D_{\alpha'\beta}(k''t'', k't') - \delta_{\alpha\beta} \delta_{kk'} \delta(t - t'),
\]
where
\[
\Pi_{\alpha\alpha'}(kt, k't') \equiv \Pi_{\alpha\alpha'}(kt, k't') + \sum_{c=1}^{4} \Pi_{(c)\alpha\alpha'}(kt, k't').
\]
Neglecting the kinetic energy terms \( \hat{T}_{mpn}^{''}, \hat{T}_{cuv}^{''} \) and \( \hat{T}_{cuv}^{'} \) in the Hamiltonian given by Eq. \[39\] leads to Eq. \[51\] with \( \Pi_{(c)\alpha\alpha'}(kt, k't') = 0 \) for all \( c \) and thus \( \Pi_{\alpha\alpha'}(kt, k't') = \Pi_{\alpha\alpha'}(kt, k't') \). In other words, all the effects of the mass polarization, Coriolis and vibrational-rotational coupling terms on the EOM of the function \( D_{\alpha\beta}(kt, k't') \) are hidden in the SE’s \( \Pi_{(c)\alpha\alpha'}(kt, k't') \). We also write the EOM for the momentum-displacement and momentum-momentum Green’s functions since these functions are in general needed in the calculation of the total energy, see Appendix \[D\] in order to use the functional derivative technique we add the following potential to the external potential part of the Hamiltonian
\[
\sum_{k=1}^{N_a-1} \sum_{\beta=1}^{3} P_{\beta}(kt) \hat{p}_{\beta}(kt).
\]
We note that this term would appear in the EOM of \( \langle \hat{u}_\alpha(kt) \rangle \), but would not appear in the corresponding equations of \( D_{\alpha\beta}(kt, k't') \). We start by writing the EOM for momentum ensemble average, namely
\[
\frac{\partial}{\partial t} \langle \hat{p}_\alpha(kt) \rangle = K_\alpha(kt) + K^{(2)}_\alpha(kt) - J_\alpha(kt).
\]
By taking a functional derivative of Eq. \[52\] with respect to \( P_\beta(k't') \) we find that
\[
\frac{\partial}{\partial t} D^{pu}_{\alpha\beta}(kt, k't') = K^{u}_{\alpha\beta}(kt, k't') + K^{''}_{\alpha\beta}(kt, k't'),
\]
where
\[
D^{pu}_{\alpha\beta}(kt, k't') = \frac{\delta \langle \hat{p}_\alpha(kt) \rangle}{\delta P_\beta(k't')},
\]
\[
K'_{\alpha\beta}(kt, k't') = \frac{\delta K_\alpha(kt)}{\delta P_\beta(k't')},
\]
\[
K''_{\alpha\beta}(kt, k't') = \frac{\delta K^{(2)}_\alpha(kt)}{\delta P_\beta(k't')}.
\]
Next we take a functional derivative of Eq. \[54\] with respect to \( J_\beta(k't') \) and write
\[
\frac{\partial}{\partial t} D^{pu}_{\alpha\beta}(kt, k't') = -\delta_{\alpha\beta} \delta_{kk'} \delta(t - t') + K_{\alpha\beta}(kt, k't')
+ K^{(2)}_{\alpha\beta}(kt, k't'),
\]
where Eq. \[39\] was used and \( D^{pu}_{\alpha\beta}(kt, k't') \equiv \frac{\delta \langle \hat{p}_\alpha(kt) \rangle}{\delta J_\beta(k't')} \). We can use Eq. \[50\] and write Eq. \[57\] as
\[
\frac{\partial}{\partial t} D^{pu}_{\alpha\beta}(kt, k't') = -\sum_{k''\cdot\alpha'} \int dt'' \Pi_{\alpha\alpha'}(kt, k''t'') D_{\alpha'\beta}(k''t'', k't') - \delta_{\alpha\beta} \delta_{kk'} \delta(t - t'),
\]
where
\[
\Pi_{\alpha\alpha'}(kt, k't') \equiv \Pi_{\alpha\alpha'}(kt, k't') + \Pi^{(2)}_{\alpha\alpha'}(kt, k't').
\]
Moreover, we have
\[
D^{pu}_{\alpha\beta}(kt, k't') = \frac{\delta \langle \hat{p}_\alpha(kt) \rangle}{\delta J_\beta(k't')} = \frac{\delta \langle \hat{u}_\beta(kt') \rangle}{\delta P_\alpha(kt)}
\equiv D^{pu}_{\beta\alpha}(k't', kt).
\]
From Eq. \[58\] we see that provided we have the necessary SE’s and the solution for \( D_{\alpha\beta}(kt, k't') \), then we can obtain \( D^{pu}_{\alpha\beta}(kt, k't') \) without solving the EOM for it.

So far our derivation is general and we have not made any simplifying assumptions. We still use the full Hamiltonian without expanding in displacements \( \hat{u} \), which is the usual procedure in the existing formulations. We can actually write the exact ensemble average of the Hamiltonian in terms of the quantities appearing in the EOM, see Appendix \[D\]. With the Hamiltonian being of general form, we leave the opportunity to use other methods, rather than expanding the Hamiltonian to a Taylor series, in writing the quantities involved such as established in Ref. \[46\]. We have obtained an exact Green’s function theory of an arbitrary system of electrons and nuclei given the Hamiltonian of kinetic energies and Coulombic interactions. With some choices of \( \mathbf{F} (\mathbf{r}, \mathbf{R}''') \) we may assume the nuclei to be distinguishable, see Sec. \[III\]. The full solution is probably rather difficult to obtain and approximations are needed. We discuss a special case of crystalline solids in Sec. \[VIII\] and give an explicit approximate expression for the Fourier transformed SE \( \Pi_{\alpha\alpha'}(k, k', \omega) \) in Sec. \[VIII\].

V. HEDIN’S EQUATIONS

In order to derive the Hedin like equations, we rewrite Eq. \[62\] by using the result
\[
\left\{ \mathcal{T} \left\{ \langle \hat{n}(r'') \hat{\psi}^\dagger(r') \hat{\psi}(r') \rangle \right\} \right\}
= \frac{\partial}{\partial t} \left\{ \mathcal{T} \left\{ \langle \hat{\psi}^\dagger(r') \hat{\psi}(r') \rangle \right\} \right\}
= \frac{\delta U(r''t)}{\delta \langle \hat{n}(r''t) \rangle}
+ \mathcal{T} \left\{ \langle \hat{\psi}^\dagger(r') \hat{\psi}(r') \rangle \langle \hat{n}(r''t) \rangle \right\}.
\]
where the vertex function is defined as

\[ \frac{\delta G(1,2)}{\delta U(3)} = \int d4 \int d5 \int d6 \delta G(1,4) \Gamma(4,5,6) \times \epsilon^{-1}(6,3) G(5,2), \]  

where the screened Coulombic interaction is defined as

\[ \delta G(1,2) = \delta(1-2) + S(1,2). \]  

We start with the vertex function defined by Eq. 64. We then invert Eq. 40 such that we have

\[ \Gamma(4,5,6) = -\delta G^{-1}(4,5) \delta V_{tot}(6), \]  

and the inverse of the dielectric function is

\[ \epsilon^{-1}(1,2) = \delta(1-2) + \int d3 v(1,3) \frac{\delta(\hat{n}(3))}{\delta U(2)}. \]  

After using Eqs. 63 and 65 in Eq. 62 we obtain again the EOM given by Eq. 10 but this time the SE, \( \Sigma(1,2) \), is given by (which is equivalent to the SE appearing in Eq. 38)

\[ \Sigma(1,4) = i\hbar \int d3 \int d5 W(1,5) G(1,3) \Gamma(3,4,5), \]  

where the screened Coulombic interaction is defined as

\[ W(1,6) \equiv \int d3 v(1,3) \epsilon^{-1}(6,3). \]  

Next we set out to derive the remaining Hedin's equations\textsuperscript{40,48,50,60,61} in order to obtain determining equations for the quantities like \( \Gamma(1,2,3) \) and \( W(1,2) \). We start with the vertex function defined by Eq. 64. We denote

\[ h' (1) \equiv i\hbar \frac{\partial}{\partial t_1} + \frac{\hbar^2}{2m_e} \nabla^2_{r_1} - V_{tot}(1), \]  

and then invert Eq. 40 such that we have

\[ G^{-1}(1,2) = h'(1) \delta(1-2) - \Sigma(1,2). \]  

By taking a functional derivative of Eq. 64 with respect to \( V_{tot}(3) \) we find that

\[ \Gamma(1,2,3) = \delta(1-2) \delta(1-3) + \frac{\delta \Sigma(1,2)}{\delta V_{tot}(3)}, \]  

where the definition of \( \Gamma(1,2,3) \) was used. Next we use

\[ \frac{\delta \Sigma(1,2)}{\delta V_{tot}(3)} = \int d4 \int d5 \frac{\delta \Sigma(1,2)}{\delta G(4,5)} \frac{\delta G(4,5)}{\delta V_{tot}(3)}, \]  

and

\[ \frac{\delta G(4,5)}{\delta V_{tot}(3)} = \int d6 \int d7 G(4,6) \Gamma(6,7,3), \]  

in Eq. 70 and write

\[ \Gamma(1,2,3) = \delta(1-2) \delta(1-3) + \int d4 \int d5 \int d6 \int d7 \times \frac{\delta \Sigma(1,2)}{\delta G(4,5)} G(4,6) G(7,5) \Gamma(6,7,3). \]  

Next we consider the screened Coulombic interaction given by Eq. 67 written as

\[ W(1,2) = v(1,2) + \int d3 \int d4 v(2,3) P_e(3,4) W(1,4) + \int d3 \int d4 v(1,3) \frac{\delta(\hat{n}_e(4))}{\delta U(3)} v(2,4), \]  

where the electronic polarization is defined as

\[ P_e(1,2) = -i\hbar \frac{\delta G(1,1^+)}{\delta V_{tot}(2)}. \]  

By making use of the result given by Eq. 72 we find that the electronic polarization satisfies

\[ P_e(1,2) = -i\hbar \int d3 \int d4 G(1,3) \Gamma(3,4,2). \]  

We rewrite now \( W(1,2) \) in terms of electron and nuclei parts. In order to achieve this we write

\[ \frac{\delta \hat{n}_n(2)}{\delta U(1)} = -\frac{i}{\hbar} \langle T \{ \Delta \hat{n}_n(2) \Delta \hat{n}_e(1) \} \rangle + D(2,1), \]  

where \( \Delta \hat{n}_n(2) \equiv \hat{n}_n(2) - \langle \hat{n}_n(2) \rangle \), \( \Delta \hat{n}_e(1) \equiv \hat{n}_e(1) - \langle \hat{n}_e(1) \rangle \) and the so-called nuclear density-density correlation function is defined as

\[ D_n(1,2) = -\frac{i}{\hbar} \langle T \{ \Delta \hat{n}_n(1) \Delta \hat{n}_n(2) \} \rangle. \]

Suppose that \( \hat{n}_n^{(p)}(1) = \hat{n}_n(1) \) for some \( p \) in the external potential part of the Hamiltonian, then

\[ \frac{\delta \hat{n}_n(1)}{\delta U_p(2)} = D_n(1,2) + \int d3 \int d4 P_e(1,3) v(3,4) \frac{\delta \hat{n}_e(4)}{\delta U_p(2)}. \]

By using

\[ \epsilon_e(1,2) \equiv \delta(1-2) - \int d3 P_e(1,3) v(3,2), \]  

we rewrite Eq. 79 as

\[ \frac{\delta \hat{n}_n(1)}{\delta U_p(2)} = \frac{\delta \hat{n}_n(2)}{\delta U(4)} = \int d5 \epsilon_e^{-1}(4,5) D_n(5,2). \]  

By using Eq. 81 in Eq. 73

\[ W(1,2) = v(1,2) + \int d3 \int d4 v(2,3) P_e(3,4) W(1,4) + \int d4 \int d5 W_e(1,5) D_n(5,4) v(2,4). \]
where we used
\[ W_e (1, 5) \equiv \int d3 \int d4 \varepsilon_e^{-1} (3, 5). \]  (83)

Finally, after some re-arranging, Eq. \( \underline{82} \) can be written as
\[ W (1, 2) = W_e (1, 2) + W_{ph} (1, 2), \]  (84)
where
\[ W_{ph} (1, 2) \equiv \int d3 \int d4 \varepsilon_e^{-1} (3, 1), \]
\[ c_e (1, 2) = \delta (1 - 2) - \int d3 \varepsilon_e (1, 3) P_c (3, 2). \]  (86)

By using Eq. \( \underline{84} \) in Eq. \( \underline{66} \) we see that the SE can be written as\( \Sigma (1, 4) = \Sigma_e (1, 4) + \Sigma_{ph} (1, 4), \) where
\[ \Sigma_e (1, 4) = i \hbar \int d3 \int d5 W_e (1, 5) G (1, 3) \Gamma (3, 4, 5), \]
\[ \Sigma_{ph} (1, 4) = i \hbar \int d3 \int d5 W_{ph} (1, 5) G (1, 3) \Gamma (3, 4, 5). \]  (87)

To summarize, the set of equations for the electron Green’s function and the related quantities in the form of Hedin’s equations are (Eqs. \( \underline{75} \underline{66} \underline{73} \underline{66} \underline{84} \) and \( \underline{87} \))
\[ G (1, 2) = G_0 (1, 2) + \int d3 \int d4 G_0 (1, 3) \Sigma_e (3, 4) G (4, 2), \]
\[ \Gamma (1, 2, 3) = \delta (1 - 2) \delta (1 - 3) + \int d4 \int d5 \int d6 \int d7 \times \delta \Sigma_e (1, 2) G (4, 5) G (7, 5) \Gamma (6, 7, 3), \]
\[ W (1, 2) = W_e (1, 2) + W_{ph} (1, 2), \]
\[ P_c (1, 2) = - i \hbar \int d3 \int d4 G (1, 3) G (4, 1^+) \Gamma (3, 4, 2), \]
\[ \Sigma (1, 4) = \Sigma_e (1, 4) + \Sigma_{ph} (1, 4). \]  (88)

Formally, the present theory is similar to the conventional ones\( \underline{40} \underline{45} \) and thus many of the approximations, like the GW-approximation\( \underline{10} \underline{01} \underline{44} \) or other suitable approximations\( \underline{56} \), can be established in a similar way than in existing Green’s function theory for electrons within the BO approximation. Namely, in the GW-approximation \( \Gamma (1, 2, 3) \approx \delta (1 - 2) \delta (1 - 3) \) and the electronic polarization and SE become \( P_c (1, 2) \approx - i \hbar G (1, 2) G (2, 1^+) \) and \( \Sigma (1, 2) \approx i \hbar W (1, 2) G (1, 2). \) The nuclei problem enters to the electronic equations, for instance, through the SE’s and the nuclei density-density correlation function \( D_n (1, 2). \) We can obtain an approximate form of \( \hat{n}_n (1) \) and thus of \( D_n (1, 2) \) by expanding the nuclei densities to a Taylor series in displacements and taking into account the terms of various order. It thus follows that in order to evaluate the expanded \( \langle \hat{n}_n (1) \rangle \) and \( D_n (1, 2), \) we need to evaluate ensemble averages like \( \langle \hat{u}_n (kt) \hat{u}_\beta (k't) \rangle. \) Similar terms appear if we expand the nuclei terms included to the SE’s \( \Sigma_c (1, 2). \) In order to determine these quantities, we can use the EOM for the nuclei Green’s functions derived in Sec. \( \underline{14} \).

Next we give explicit and approximate expressions for the corresponding SE’s arising from the Coriolis and vibrational-rotational coupling terms. The quantities \( S_c (rt, r't') \) appearing in Eq. \( \underline{37} \) are defined as
\[ S_1 (rt, r't') = - \frac{1}{i \hbar} \frac{\hbar^2}{M_{nuc}} \int dr'' \nabla_r \cdot \nabla_{r''} \times \langle \hat{T} \{ \hat{u}_e (r't') \hat{\psi} (rt) \hat{\psi}^\dagger (r't') \} \rangle, \]
\[ S_2 (rt, r't') = \frac{1}{i \hbar} \sum_{\beta, \gamma} \frac{\partial}{\partial \gamma} \times \langle \hat{T} \{ \hat{D}_{\beta \gamma} (t) \hat{\psi} (rt) \hat{\psi}^\dagger (r't') \} \rangle, \]
\[ S_3 (rt, r't') = \frac{2}{i \hbar} \sum_{\beta, \gamma} \frac{\partial^2}{\partial \gamma^2} \times \langle \hat{T} \{ \hat{\psi} \hat{\psi}^\dagger \hat{\psi} (r't') \} \rangle, \]  (89)

where
\[ \hat{D}_{\beta \gamma} (t) \equiv \hat{L}_{\beta \gamma}^{(1)} (t) + \sum_{k=1}^{N_{nuc} - 1} \sum_{\alpha} \hat{L}_{\alpha \beta \gamma}^{(2)} (k) \hat{p}_\alpha (k). \]  (90)

Perhaps among the simplest approximations to the SE’s \( \Sigma_c (rt, r't') \) can be obtained if we write
\[ S_1 (rt, r't') = - i \frac{\hbar^2}{M_{nuc}} \int dr'' \nabla_r \cdot \nabla_{r''} \times G_2 (r't', rt, r'' t'), \]
\[ S_2 (rt, r't') \approx \sum_{\beta, \gamma} \frac{\partial}{\partial \gamma} \langle \hat{D}_{\beta \gamma} (t) \rangle G (rt, r't'), \]
\[ S_3 (rt, r't') \approx - \frac{2 \hbar}{i} \sum_{\beta, \gamma, \sigma} \frac{\partial^2}{\partial \gamma^2} \times \langle \hat{\psi} \hat{\psi}^\dagger \rangle G_2 (r'' t', rt, r't'), \]  (91)

where
\[ G_2 (1, 2, 1', 2') \equiv - \frac{1}{R} \langle \hat{T} \{ \hat{\psi} (1) \hat{\psi} (2) \hat{\psi}^\dagger (2') \hat{\psi}^\dagger (1') \} \rangle. \]  (92)

Similar approximation is established in Sec. \( \underline{17} \) when we approximate \( \langle \hat{u}_{\alpha_1} (kt) \hat{u}_n (rt) \rangle \approx \langle \hat{u}_{\alpha_1} (kt) \rangle \langle \hat{u}_n (rt) \rangle. \) If we further make the Hartree-Fock approximation\( \underline{42} \)
\[ G_2 (1, 2, 1', 2') \approx G (1, 1') G (2, 2') - G (1, 2') G (2, 1'), \]  (93)
we find by using Eq. (88) that

\[
\Sigma_1 (\mathbf{r}_t, \mathbf{r}_t'' t'') = \frac{h^3}{\hbar \cdot M_{\text{mac}}} \int d\mathbf{r} \nabla_r \cdot \nabla_\mathbf{r} \left[ \delta (\mathbf{r} - \mathbf{r}'') G (\mathbf{r}_t, \mathbf{r}_t) - G (\mathbf{r}_t, \mathbf{r}_t) \delta (t - t'') \right],
\]

\[
\Sigma_2 (\mathbf{r}_t, \mathbf{r}_t'' t'') = \sum_{\beta, \gamma} \left( \hat{\mathcal{D}}_{\beta \gamma}^{(3)} (t) \right) r_\gamma \frac{\partial}{\partial r_\beta} \delta (\mathbf{r} - \mathbf{r}'') \delta (t - t''),
\]

(94)

and

\[
\Sigma_3 (\mathbf{r}_t, \mathbf{r}_t'' t'') = 2i h \sum_{\beta, \sigma, \gamma, \gamma'} \left( \hat{\mathcal{L}}_{\sigma \gamma \gamma'}^{(3)} \right) \int d\mathbf{r} r_\gamma r_{\gamma'} \frac{\partial^2}{\partial r_\beta \partial r_\beta} \delta (\mathbf{r} - \mathbf{r}'') - G (\mathbf{r}_t, \mathbf{r}_t) \delta (t - t'').
\]

(95)

After Taylor expanding $\hat{\mathcal{D}}_{\beta \gamma}^{(3)} (t)$ and $\hat{\mathcal{L}}_{\sigma \gamma \gamma'}^{(3)}$ in displacements $\mathbf{u}$, $\Sigma_2 (1, 2)$ and $\Sigma_3 (1, 2)$ become functions of $\langle \hat{u}_\alpha (k) \rangle$, $D_{\alpha \beta}^{(3)} (kt, k't')$ and so on.

Before continuing we give an overview of a work flow how the coupled set of electrons and nuclei could be solved. First we give an initial guess for the rest positions $\mathbf{x}$ as described in Sec. VI. Given the rest positions we expand all the quantities in the Hedin’s equations, which are functions of the nuclei variables, to a Taylor series in $\mathbf{u}$. In the first iteration, we retain only the zeroth order terms meaning that $W_{ph} (1, 2) = 0$ from which follows that $W (1, 2) = W_e (1, 2)$ and $\Sigma (1, 2) = \Sigma_e (1, 2)$ (see Eq. 88). With the preceding choices, the Hedin’s equations are actually similar to those in the BO approximation, but here written in the body-fixed frame. The zeroth order approximations for the SE’s $\Sigma_e (1, 2)$ can be obtained by using the relations given by Eqs. 88 and 77. After the Hedin’s equations are solved, we can calculate the nuclei SE by using the quantities obtained from the solution of the Hedin’s equation, see for instance Eq. 113. Given the nuclei SE, the EOM for the nuclei Green’s function can be solved. Provided we have obtained the nuclei Green’s function, we can write the Hedin’s equation with non-zero $W_{ph} (1, 2)$ and solve the Hedin’s equation with the SE $\Sigma (1, 2) = \Sigma_e (1, 2) + \Sigma_{ph} (1, 2)$. After the new solutions of the electron and nuclei Green’s functions have been obtained, we can test whether or not the rest positions $\mathbf{x}$ are equilibrium positions (see Sec. VI). We iterate as long as we have found the equilibrium positions. Provided we have found the equilibrium positions, we seek the solution of the coupled equations such that the grand potential, or in the case of zero temperature formalism, the total energy is minimized. In the case when we have several configurations for which the rest positions are equilibrium positions, the aim is to find those equilibrium positions which minimize the grand potential (or the total energy).

VI. DETERMINATION OF REST POSITIONS

We have not yet discussed in detail how to determine the rest positions $\mathbf{x}$ and so far these quantities have been considered as arbitrary parameters. Consider, for instance, the total energy of the system, $E_{\text{tot}}$, defined as an ensemble average of the Hamiltonian

$$E_{\text{tot}} = \left\langle \hat{H} \right\rangle.$$  (96)

The value of $E_{\text{tot}}$ must be independent of $\mathbf{x}$ provided our expansion (in displacements $\mathbf{u}$) of the SE’s, or the Hamiltonian ensemble average itself, converges for a given $\mathbf{x}$. Hence, in principle we should have the value of $E_{\text{tot}}$ the same for any given and reasonable $\mathbf{x}$. However, we are probably not able to make such an expansion up to arbitrary order in $\mathbf{u}$ and thus the value of $E_{\text{tot}}$ may become dependent on $\mathbf{x}$ due to the approximations established. For instance, if the positions $\mathbf{x}$ are chosen far away from the positions around which the nuclei would vibrate, then in order to calculate the reasonable values of $E_{\text{tot}}$, the displacements $\mathbf{u}$ would be rather large. This implies that we would need a rather high order Green’s functions for nuclei or alternatively a rather high order expression for the nuclei SE to describe the system properly. If we choose the positions $\mathbf{x}$ rather poorly and at the same time take only the lowest order quantities in $\mathbf{u}$ into account, we expect to find rather unrealistic results. Even though our theory is generally valid and we do not even need to have the nuclei to vibrate around some particular region of space, it is beneficial to have some consistent strategy to obtain the parameters $\mathbf{x}$ such that the systems in which the nuclei perform such rather small vibrations around some regions of space we can describe the system with a reasonable accuracy by using the approximations of lower orders in $\mathbf{u}$.

For the aforementioned systems, like some stable crystal lattices, we use the following method to determine the positions $\mathbf{x}$. The initial value of the $\mathbf{x}$ is obtained in the same way as within the BO approximation, that is, from the experimental data of known structures or in the case of hypothetical structures by using the methods of structural chemistry. After the initial guess, we aim to find the positions $\mathbf{x}$ such that they are equal to the most probable positions of the nuclei, that is, we seek the positions such that

$$\mathbf{x}_k = \left\langle \mathbf{R}_k' \right\rangle = \mathbf{x}_k + \left\langle \hat{\mathbf{u}}_k \right\rangle.$$  (97)

We note that $\left\langle \hat{\mathbf{u}}_k \right\rangle$ is a function of $\mathbf{x}$ since the Hamiltonian is and if the external potentials vanish, $\left\langle \mathbf{R}_k' \right\rangle$ is independent of time. If Eq. 97 holds, then it follows that $\langle \hat{\mathbf{u}}_k \rangle = 0$. That is, if we are able to choose the positions $\mathbf{x}$ as in Eq. 97, then the expected values of the displacements vanish. Next we seek a way how to find the displacements satisfying $\langle \hat{\mathbf{u}}_k \rangle = 0$ and thus the rest positions $\mathbf{x}$ satisfying Eq. 97. For some systems, like
Appendix D) and retain only the lowest orders. After calculating the commutators, we obtain to the lowest orders in displacements

\[ K_0(kt) \approx -\frac{\partial V_{nn}(\mathbf{x})}{\partial x_1(kt)} - \int d\mathbf{r} \sum_{k_1,\alpha_1} \frac{\partial^2 V_{en}(\mathbf{r}, \mathbf{x})}{\partial x_{\alpha_1}(k_1) \partial x_{\alpha_2}(k_2)} \langle \hat{u}_{\alpha_1}(k_1) \hat{u}_{\alpha_2}(k_2) \rangle \cdot \]
and from the solutions of these equations we obtain the quantities like \( G(t, r, r') \), \( P_e(t, r, r') \), \( W_e(t, r, r') \) and \( D^T_{jk}(k, k't) \) and we can check whether or not Eq. 102 holds and indicates that we have found the positions such that Eq. 97 is satisfied.

### VII. NUCLEI RELATED CONSIDERATIONS

#### A. Nuclei vibrations

We start by writing the nuclei EOM in frequency space, but before Fourier transforming, all the time-dependent potentials are set equal to zero. It follows that the nuclei Green’s function and the nuclei SE are then functions of time differences only and we can write Eq. 51 in terms of Fourier transformed quantities as (the convention used is given in Appendix A)

\[
\delta_{\alpha\beta}\delta_{kk'} = \sum_{k',\alpha'} [M_{kk'}^2\delta_{\alpha\alpha'}\delta_{kk'} - \Pi'_{\alpha\alpha'}(k, k', \omega)] \times D_{\alpha\beta}(k', k; \omega). 
\]

We write Eq. 108 in matrix form and re-arrange such that

\[
\mathbf{D}(\omega) = [\omega^2\mathbf{I} - \mathbf{C}(\omega)]^{-1}, \tag{109}
\]

where \( \mathbf{D}(\omega) \equiv \mathbf{M}^{1/2}\mathbf{D}(\omega)\mathbf{M}^{1/2} \) and \( \mathbf{C}(\omega) \equiv \mathbf{M}^{-1/2}\mathbf{\Pi}'(\omega)\mathbf{M}^{-1/2} \). The components of these matrices are denoted by \( \alpha \) and \( \beta \). Next we write the SE as \( \mathbf{C}(\omega) = \mathbf{C}^A + \mathbf{C}^{NA}(\omega) \) and assume that \( \mathbf{C}^A \) is the Hermitian part of \( \mathbf{C}(\omega) \), which we assume to be independent of frequency and \( \mathbf{C}^{NA}(\omega) \) the non-Hermitian part of \( \mathbf{C}(\omega) \). One possible choice is \( \mathbf{C}^A = \mathbf{C}^N(0) \) and \( \mathbf{C}^{NA}(\omega) = \mathbf{C}(\omega) - \mathbf{C}^N(0) \) such that we collect all the Hermitian zero frequency contributions of \( \mathbf{C}^N(\omega) \) to \( \mathbf{C}^N(0) \). For a Hermitian matrix, we can find a complete and orthonormal set of eigenvectors satisfying

\[
\hat{\omega}_{\alpha}^2v_{\alpha}(k|j) = \sum_{k',\beta}^{\mathbf{C}^A} (kk') v_{\beta}(k'|j),
\]

\[
\delta_{jj'} = \sum_{\alpha} v_{\alpha}(k|j) v_{\alpha}^*(k'|j),
\]

\[
\delta_{\alpha\beta}\delta_{kk'} = \sum_{\alpha} v_{\alpha}(k|j) v_{\alpha}^*(k'|j). \tag{110}
\]

We call the quantities \( \hat{\omega}_{\alpha} \) the adiabatic normal mode frequencies. The eigenvalues \( \omega_{\alpha}^2 \) are real since \( \mathbf{C}^A \) is Hermitian and \( \hat{\omega}_{\alpha} \) are real if \( \mathbf{C}^A \) is positive definite. We transform Eq. 109 by using the eigenvectors of \( \mathbf{C}^A \) such that

\[
\mathbf{D}(\omega) = [\omega^2\mathbf{I} - \hat{\omega}^2 - \mathbf{C}^{NA}(\omega)]^{-1}, \tag{111}
\]

where \( \mathbf{D}(\omega) \equiv \mathbf{v}^\dagger\mathbf{D}(\omega)\mathbf{v} \) and \( \mathbf{C}^{NA}(\omega) \equiv \mathbf{v}^\dagger\mathbf{C}^{NA}(\omega)\mathbf{v} \). If \( \mathbf{C}^{NA}(\omega) \) is sufficiently small, the quasi-particle picture holds and \( \mathbf{C}^{NA}(\omega) \) can be pictured in generating interactions between adiabatic normal modes by shifts of their values and finite lifetimes (imaginary part of \( \mathbf{C}^{NA}(\omega) \)). Correct treatment requires the continuation of the frequency variable to the complex frequency plane. The usual procedure is to consider the Matsubara Green’s functions continued to the complex frequency plane. However, we can also obtain the Green’s function of complex frequency by just replacing the real frequency \( \omega \) by the complex one \( \omega \).

We point out that the present discussion is general without any approximations made. We establish a similar consideration of vibrations by using phonon basis in Sec. 8.14.17,20,74.

### VII. A. Nuclei self-energy

In order to have an approximate form for the SE \( \Pi_{\alpha\alpha'}(k, k', \omega) \), we start by giving explicit form for some of the terms included in \( K_{\alpha\beta'}(k, k't) \) given by Eq. 49. We have already calculated the commutators included to the lowest orders in \( \tilde{u}_\alpha(k) \) and we can obtain \( K_{\alpha\beta'}(k, k't) \) by taking a functional derivative of \( K_\alpha(k) \) given by Eq. 103 with respect to \( J_\beta(k't) \), namely

\[
K_{\alpha\beta}(k, k't) = -\sum_{k',\alpha',\beta} \frac{\partial^2 V_{\alpha\alpha'}(x)}{\partial x_{\alpha'}(k)\partial x_{\alpha'}(k')} D_{\alpha\beta}(k't, k'),
\]

\[
-\int dr \frac{\partial^2 V_{\alpha'}(r, x)}{\partial x_{\alpha'}(k)\partial x_{\alpha'}(k')} \frac{\delta(u_{\alpha'}(k't) n_e(r))}{\delta J_\beta(k't)} - \int dr \frac{\partial V_{\alpha'}(r, x)}{\partial x_{\alpha'}(k)} \frac{\delta n_e(r)}{\delta J_\beta(k't)} + O(n^2_e). \tag{112}
\]

Actually, the terms visible in Eq. 112 are all the terms included in \( K_{\alpha\beta'}(k, k't) \) if the Hamiltonian is expanded in displacements up to second order before writing the EOM. This is the usual procedure in the earlier laboratory frame formulations. Next we use the following result

\[
\frac{\delta(n_e(r))}{\delta J_\beta(k't')} = \int dr_2 \int dt_2 \int dr_3 \int dt_3 P_e(rt, r_3 t_3) \tilde{W}_e(r_3 t_3, r_2 t_2) \frac{\delta(n_e(r_2 t_2))}{\delta J_\beta(k't')} \tag{113}
\]

where \( \tilde{e}_e(r_1 t_1, r_2 t_2) \) and \( \tilde{W}_e(r_3 t_3, r_2 t_2) \) are given by Eqs. 80 and 83 respectively. These quantities can be obtained from the solution of the Hedin’s equations. We also write for the quantity in the second term on the right hand side of Eq. 112

\[
\frac{\delta(u_{\alpha_1}(k_1 t) n_e(r))}{\delta J_\beta(k't')} = i\hbar \frac{\delta^2 (\tilde{n}_e(r))}{\delta J_\beta(k't') \delta J_{\alpha_1}(k_1 t)} + (\tilde{u}_{\alpha_1}(k_1 t) n_e(r)) \frac{\delta (\tilde{n}_e(r))}{\delta J_\beta(k't')} + (\tilde{n}_e(r)) D_{\alpha_1\beta}(k_1 t, k't'). \tag{114}
\]
Finally, by using Eqs. [112][114] in Eq. [50] we can write for the nuclei SE under consideration in frequency space
\[\Pi_{\alpha\beta}(k, k', \omega) = \frac{\partial^2 V_{nn} (x)}{\partial x_{\alpha}(k) \partial x_{\beta}(k')} + \int \text{d}r \frac{\partial^2 V_{en} (r, x)}{\partial x_{\alpha}(k) \partial x_{\beta}(k')} \langle \hat{n}_e (r) \rangle + \int \text{d}r \int \text{d}r' \frac{\partial n_{n0} (x, r)}{\partial x_{\alpha}(k)} \left[ \hat{W}_e (r, r', \omega) - v (r, r') \right] \times \left[ \frac{\partial n_{n0} (x, r')}{\partial x_{\beta}(k')} + \sum_{k_1, \alpha_1} \frac{\partial^2 n_{n0} (x, r')}{\partial x_{\alpha_1}(k_1) \partial x_{\beta}(k')} \langle u_{\alpha_1} (k_1) \rangle \right] + \sum_{k_1, \alpha_1} \int \text{d}r \int \text{d}r' \frac{\partial^2 n_{n0} (x, r)}{\partial x_{\alpha}(k) \partial x_{\alpha_1}(k_1)} \times \left[ \hat{W}_e (r, r', \omega) - v (r, r') \right] \langle \hat{u}_{\alpha_1} (k_1) \rangle \times \left[ \frac{\partial n_{n0} (x, r')}{\partial x_{\beta}(k')} + \sum_{k_2, \alpha_2} \frac{\partial^2 n_{n0} (x, r')}{\partial x_{\alpha_2}(k_2) \partial x_{\beta}(k')} \langle u_{\alpha_2} (k_2) \rangle \right] + \cdots \right].

(115)

In Eq. [115] \(\hat{W}_e (r, r', \omega)\) is the Fourier transform of Eq. [83] in the relative time variable. Terms explicitly shown in Eq. [113] are already included in the harmonic approximation, which means that the Hamiltonian is expanded up to second order in displacements (before writing the EOM). Actually not all the terms in the harmonic approximation are even visible in Eq. [115]. Namely, the first term on the right hand side of Eq. [114] is not shown and in practise this means that we have approximated \(\langle \hat{u}_{\alpha_1} (k_1 t) \hat{u}_e (rt) \rangle \approx \langle \hat{u}_{\alpha_1} (k_1 t) \rangle \langle \hat{u}_e (rt) \rangle\). Further, only some of the second order terms of the right hand side of Eq. [115] are included. Sometimes it is convenient to write \(\Pi_{\alpha\beta}(k, k', \omega) = \Pi_{\alpha\beta}^A (k, k') + \Pi_{\alpha\beta}^N (k, k', \omega)\). The adiabatic SE \(\Pi_{\alpha\beta}^A (k, k') = \Pi_{\alpha\beta} (k, k', 0)\) is real (at least when terms visible in Eq. [115] are taken into account) while the non-adiabatic part \(\Pi_{\alpha\beta}^N (k, k', \omega) = \Pi_{\alpha\beta} (k, k', \omega) - \Pi_{\alpha\beta} (k, k', 0)\) is complex, in general. The adiabatic SE is real since \(\hat{W}_e (rt, r' t')\) is. In the present case (Eq. [115]), the quantity \(\Pi_{\alpha\beta}^N (k, k' t')\) appearing in Eq. [119] is
\[\Pi_{\alpha\beta}^N (k, k' t') = \frac{\partial^2 V_{nn} (x)}{\partial x_{\alpha}(k) \partial x_{\beta}(k')} \delta (t - t'),
\]
while the rest of the Fourier transforms of the terms visible in Eq. [115] are included to \(\Pi_{\alpha\beta}^N (k, k' t')\). For a better comparison with the existing theory, we use Eq. [112] and write the non-adiabatic contribution as
\[\Pi_{\alpha\beta}^N (k, k', \omega) = \int \text{d}r \int \text{d}r' \frac{\partial n_{n0} (x, r)}{\partial x_{\alpha}(k)} \times \left[ \hat{W}_e (r, r', \omega) - \hat{W}_e (r, r', 0) \right] \times \frac{\partial n_{n0} (x, r')}{\partial x_{\beta}(k')} + \cdots ,
\]
where terms including the quantity \(\langle \hat{u}_e (k) \rangle\) are not explicitly shown. Provided we can choose the parameters \(x\) such that Eq. [97] holds, then terms involving the quantities \(\langle \hat{u}_e (k) \rangle\) vanish, see Sec. [11] The relation given by Eq. [117] is formally analogous with the result obtained earlier. However, the difference is in the densities \(n_{n0} (x, r')\) (see Eq. [112]) and here all the variables are in the body-fixed frame. We note that if necessary, the higher order expressions for the nuclei and phonon SE’s can be obtained by systematically including higher order terms in the expansion of \(K_{\alpha\beta} (kt, k't')\). Related to this, some results of a recent study on generic electron-boson Hamiltonians may be useful within the present theory as well.

Even though we are not giving explicit expressions for the SE’s \(\Pi_{\alpha\alpha}^N (kt, k't')\), these quantities can be obtained with the same procedure as established here for \(\Pi_{\alpha\alpha}^N (kt, k't')\). Namely, calculate the commutators contained in \(K_{\alpha\beta} (kt)\) (Eq. [37]) by expanding the quantities involved in \(\hat{u}\), take the functional derivative with respect to \(J_3 (k't')\) in order to obtain \(K_{\alpha\beta} (kt, k't')\) and then use Eq. [50] to obtain \(\Pi_{\alpha\alpha}^N (kt, k't')\). In obtaining these expressions, similar approximations may be established as we did in the case of \(\Pi_{\alpha\alpha} (kt, k't')\).

VIII. CRYSTALLINE SOLIDS

Here we apply the general theory to crystalline solids. First of all, the electron and nuclei mass polarization terms \(T_{\text{me}}\) and \(T_{\text{mn}}\) and also \(T_{\text{crv}}\) appearing in the transformed kinetic energy are proportional to the inverse of the total nuclei mass and are thus small for crystals. Furthermore, we assume that one can find an explicit condition of the form (Eq. [13]) such that the contributions from the kinetic energy \(T_{\text{crv}}\) become small. Some justifications for their neglect have been given, when the implicit condition is chosen to be the Eckart condition given by Eq. [14]. By neglecting the aforementioned terms the EOM for electrons remain otherwise the same, except that we have \(\Sigma (1, 3) = \Sigma (1, 3)\) in Eqs. [40] and [42]. In turn, the nuclei EOM remain otherwise the same, but in Eq. [51] the SE is \(\Pi_{\alpha\alpha} (kt, k't') = \Pi_{\alpha\alpha} (kt, k't')\).

A. Phonons and their interactions

Here we use the notation \(k = l \kappa\) and so on, see Appendix [A]. The aim is to define phonon frequencies beyond the BO approximation. In the present case, Eq. [108] can be written as
\[\sum_{l', l'' \kappa', \kappa''} \left[ M_l \omega^2 \delta_{\alpha\alpha'} \delta_{\kappa\kappa'} \delta_{\kappa\kappa''} - \Pi_{\alpha\alpha'} (l \kappa, l' \kappa', \omega) \right] D_{\alpha \beta} (l'' \kappa'', l' \kappa', \omega) = \delta_{\alpha \beta} \delta_{l l'} \delta_{\kappa \kappa'}. \]
We also note that the quantities like \(D_{\alpha \beta} (l \kappa, l' \kappa', \omega)\) and \(\Pi_{\alpha \beta} (l \kappa, l' \kappa', \omega)\) are dependent only on the difference the
cell indices \( l - l' \). Therefore, we write \( D_{\alpha\beta} (l\kappa, l'\kappa', \omega) \) as a discrete Fourier transform in the relative coordinate allowed by the periodic boundary conditions, namely

\[
D_{\alpha\alpha'} (\kappa\kappa', l, \omega) = \frac{1}{N} \sum_{q} N \sum_{\alpha} D_{\alpha\alpha'} (\kappa\kappa', q, \omega) e^{i q \cdot x_l},
\]

and in a similar way for \( \Pi_{\alpha\alpha'} (\kappa\kappa', l, \omega) \). In Eq. 119 \( N \) is the number of \( q \) points and thus number of unit cells in the Born-von Karman cell. By using Eq. 119 and similar expression for \( \Pi_{\alpha\alpha'} (\kappa\kappa', l', \omega) \) in Eq. 118 we obtain

\[
\sum_{\kappa'^{\prime}, \kappa} [M_{\kappa, \omega}^2 \delta_{\alpha\alpha'} \delta_{\kappa\kappa'^{\prime}} - \Pi_{\alpha\alpha'} (\kappa\kappa'^{\prime}, q, \omega)] \
\times D_{\alpha'\beta'} (\kappa'^{\prime}\kappa', q, \omega) = \delta_{\alpha\beta} \delta_{\kappa\kappa'^{\prime}},
\]

and after some re-arranging and by using matrix notation

\[
\mathbf{D} (q, \omega) = [\omega^2 \mathbf{I} - \mathbf{C} (q, \omega)]^{-1},
\]

where

\[
\mathbf{C} (q, \omega) \equiv M^{-1/2} \Pi (q, \omega) M^{-1/2}; \\
\mathbf{D} (q, \omega) \equiv M^{1/2} \mathbf{D} (q, \omega) M^{1/2}.
\]

The components of the matrix like \( \mathbf{C} (q, \omega) \) are labeled by \( \alpha \) and \( \beta \), for instance. We establish a similar procedure as in Sec. VI, namely, we write the SE as \( \mathbf{C} (q, \omega) = C^A (q) + C^{NA} (q, \omega) \), where \( C^A (q) = C (q, 0) \) and \( C^{NA} (q, \omega) = C (q, \omega) - C (q, 0) \). The eigenvalue equation for \( C^A (q) \) can be written as

\[
\omega_{qj}^2 e_\alpha (k|qj) = \sum_{\kappa'} C^A_{\alpha\beta} (k\kappa'|q) e_\beta (k'|qj).
\]

We call the quantities \( \omega_{qj} \) the adiabatic phonon frequencies. The eigenvalue equation given by Eq. 123 is analogous to the eigenvalue equation written for the dynamical matrix in the conventional theory of lattice dynamics. As the adiabatic phonon frequencies \( \omega_{qj} \) are defined by Eq. 123, in contrast to the conventional theory, already the non-interacting phonons potentially contain the terms of the Hamiltonian of arbitrary order in \( \mathbf{u} \). In order for \( \omega_{qj}^2 \) to be positive and thus \( \omega_{qj} \) to be real, the matrix \( C^A (q) \) have to be positive definite, which is not in general the case for a given \( x \). This is also the case in the BO theory of lattice dynamics, where the positive definiteness of the dynamical matrix implies the minimum of the BO energy surface and the stability of the crystal lattice. Provided the matrix \( C^A (q) \) is Hermitian (as it is, for example, if Eq. 115 is used), the components of the eigenvector \( e_\alpha (k|qj) \) can be chosen to satisfy the orthonormality and completeness conditions

\[
\sum_{\kappa'} e_\alpha (\kappa|q'j') e^*_{\alpha} (\kappa'|qj) = \delta_{jj'}, \\
\sum_{j} e_\alpha (\kappa|qj) e^*_{\beta} (\kappa'|qj) = \delta_{\alpha\beta} \delta_{\kappa\kappa'}.
\]

We use the eigenvectors of the adiabatic SE to transform Eq. 122 to equation in phonon basis and after we establish the transformation

\[
\mathbf{D} (q, \xi) = \left[ \left[ \xi^2 - \omega_{qj}^2 \right] \mathbf{I} - \mathbf{C}^{NA} (q, \xi) \right]^{-1},
\]

where \( \mathbf{D} (q, \xi) \equiv \mathbf{e}^\dagger (q) \mathbf{D} (q, \xi) \mathbf{e} (q) \) and \( \mathbf{C}^{NA} (q, \xi) \equiv e^\dagger (q) \mathbf{C}^{NA} (q, \xi) e (q) \). We call \( \mathbf{D} (q, \xi) \) the phonon Green’s function and \( \mathbf{C}^{NA} (q, \xi) \) the non-adiabatic phonon SE. Here, \( \xi \) is the complex frequency variable. If the non-adiabatic SE vanishes, we obtain the adiabatic phonon Green’s function \( \mathbf{D}^A (q, \omega) = 1 / \left( \omega^2 - \omega_{qj}^2 \right) \) which is of the usual form appearing in the BO theory of lattice dynamics. The adiabatic phonons have infinite lifetimes if the non-adiabatic SE vanishes. The non-adiabatic part can be pictured in generating interactions between the adiabatic phonons which appear as shifts to the adiabatic eigenvalues and finite lifetimes of these quasiparticles. This picture is valid if the non-adiabatic SE is sufficiently small in comparison to the adiabatic part. If the non-diagonal terms of \( \mathbf{C}^{NA} (q, \xi) \) are relatively small such that \( C_{jj'}^{NA} (q, \xi) \approx 0 \) for all \( j \neq j' \), Eq. 125 becomes

\[
\mathbf{D}_{jj'} (q, \xi) = \frac{1}{\xi^2 - \omega_{qj}^2 - C_{jj'}^{NA} (q, \xi)},
\]

from which the shifts to the adiabatic phonon frequencies and finite lifetimes of adiabatic phonons are usually deduced. The non-adiabatic phonon SE in its general form can be written as

\[
C_{jj'}^{NA} (q, \xi) = \sum_{l, \kappa, \kappa'} \sum_{\alpha} \Pi_{\alpha}^{NA} (\kappa\kappa', l, \xi) \times e_\alpha (\kappa|qj) e^{-i q \cdot x_l}.
\]

By using Eqs. 80 and 83 in Eq. 117 and then Fourier transforming and changing the representation, we obtain the following approximate form for the non-adiabatic phonon SE

\[
\mathbf{c}_{jj'}^{NA} (q, \xi) = \frac{1}{N} \int dx \int dx' \left[ g_{qj} (r, \xi) P_e (r, r', \xi) \bar{g}_{qj'} (r') - g_{qj} (r, 0) P_e (r, r', 0) \bar{g}_{qj'} (r') \right].
\]

In Eq. 128

\[
\bar{g}_{qj} (r) = \int dr' \bar{g}_{qj} (r') \bar{c}_e^{-1} (r', r, \xi),
\]

where \( \bar{g}_{qj} (r) \) is the complex conjugate of \( \bar{g}_{qj}^* (r) \). By re-arranging Eq. 129 we find that \( g_{qj} (r, \xi) \) satisfies the following equation

\[
g_{qj} (r, \xi) = \bar{g}_{qj} (r) + \int dr' \int dr'' g_{qj} (r', \xi) P_e (r', r'', \xi) \bar{g}_{qj''} (r'') \cdot
\]

\[
\times u (r'', r).
\]
The diagrams corresponding to $\mathcal{D}(q, \xi)$, $C^{NA}(q, \xi)$ and $g_{q1}(r, \xi)$ are of a similar form as in the laboratory frame formulation and are given in Ref. 48.

**B. Momentum functions**

By establishing the approximations discussed at the beginning of this section and then comparing Eqs. 51 and 58 we see that

$$\frac{\partial}{\partial t} D_{\alpha\beta}^{\mu}(k, k') = M_k \frac{\partial^2}{\partial t^2} D_{\alpha\beta}(k, k'),$$

and thus for the Fourier transforms

$$D_{\alpha\beta}^{\mu}(k, k', \omega) = -iM_k \omega D_{\alpha\beta}(k, k', \omega).$$

Therefore, after we have obtained a solution for $D_{\alpha\beta}(k, k', \omega)$ we can also obtain $D_{\alpha\beta}^{\mu}(k, k', \omega)$. The last function we need is the momentum Green's function and in the present case Eq. 55 becomes

$$\frac{\partial}{\partial t} D_{\alpha\beta}^{pp}(k, k') = K'_{\alpha\beta}(k, k'),$$

where we approximate

$$K'_{\alpha\beta}(k, k') \approx -\sum_{k_2, \alpha_2} \frac{\partial^2 V_{en}(x)}{\partial x_\alpha(k) \partial x_{\alpha_2}(k_2)} \frac{\delta(\hat{n}_{\alpha_2}(k_2))}{\delta P_{\beta}(k', k')}$$

$$-\int dr \frac{\partial V_{en}(r, x)}{\partial x_\alpha(k)} \frac{\delta(\hat{n}_\alpha(r))}{\delta P_{\beta}(k', k')}$$

$$-\sum_{k_2, \alpha_2} \int dr \left[ \frac{\partial^2 V_{en}(r, x)}{\partial x_\alpha(k) \partial x_{\alpha_2}(k_2)} \right]$$

$$\times \frac{\delta(\hat{n}_{\alpha_2}(k_2)) \hat{n}_\alpha(r)}{\delta P_{\beta}(k', k')} + O(u^2),$$

which can be obtained directly from Eq. 103. By using the same approximations for $K'_{\alpha\beta}(k, k')$, as in Sec. VII B, we established in writing $K_{\alpha\beta}(k, k')$, we find that Eq. 133 can be written as

$$\frac{\partial}{\partial t} D_{\alpha\beta}^{pp}(k, k') = -\sum_{k', \alpha'} \int dt'' \pi_{\alpha\alpha'}(k, k', k'')$$

$$\times D_{\alpha\beta}^{pp}(k'', k', k').$$

The Fourier transform of this equation is

$$i\omega D_{\alpha\beta}^{pp}(k, k', \omega) = \sum_{k', \alpha'} \pi_{\alpha\alpha'}(k, k', \omega) D_{\alpha\beta}^{pp}(k'', k', \omega).$$

Since by Eq. 40, $D_{\beta\alpha}^{pp}(k', k) = D_{\alpha\beta}^{pp}(k, k')$, we can write

$$D_{\alpha\beta}^{pp}(k, k', \omega) = -M_k \sum_{k'', \alpha'} \pi_{\alpha\alpha'}(k, k'', \omega)$$

$$\times D_{\alpha\beta}^{pp}(k', k'', \omega),$$

where Eq. 132 was used. Now we have all the necessary equations in order to calculate the total energy of the system, for example.

**IX. CONCLUSIONS**

In this work, we derived a coupled and self-consistent set of exact equations for the electron and nuclei Green's functions following from the Hamiltonian of Coulombic interactions and kinetic energies as a starting point. The present theory, when applied to crystalline solids, resembles in many parts with the previous ones. However, we take into account an issue arising from the translational and rotational symmetry of the Hamiltonian preventing the use of the existing Green's function theories to describe systems other than those with constant density eigenstates. The present theory is formally exact and it is not limited to the harmonic approximation. Moreover, the theory developed can be applied to arbitrary molecules, which in general, were out of the range of validity of the previous theories based on the same method. The complexity of the given system of EOM is of the same order with the existing ones when applied to crystalline solids.

In addition to the general EOM, we considered the normal modes of arbitrary molecular systems, a special case of crystalline solids and reproduced the analogs of some of the results appearing in the existing theories. For instance, phonons and their interactions were defined in a rather general way. While it is probably not a realistic goal to obtain the solution of the EOM in general form in arbitrary systems, there is some work left to derive computationally accessible approximations to be used in the actual calculations. Our main emphasis in this work was on crystalline solids and we leave a more detailed treatment of molecules for future work. The present theory allows one to go beyond BO approximation in a systematic and exact way and therefore it may turn out to be useful in understanding the behaviour of non-relativistic quantum mechanical many-body systems of interacting electrons and nuclei.

**Appendix A: Notation**

The following notations are used

$$\hat{u}_{\alpha m}(k_m) \equiv \hat{u}_{\alpha 1}(k_1) \cdots \hat{u}_{\alpha m}(k_m),$$

$$\sum_{k_m, \alpha m} \sum_{k_1, \alpha_1} \cdots \sum_{k_m, \alpha_m},$$

and so on. The following notation, suitable for the description of crystalline solids, is essentially the same as Refs. 58 and 48. We denote the nuclei with the labels $k = l_k$, and write $x_k = x_{lk} = x_1 + x_{lk}$, where $x(k)$ is the position vector of the nuclei $k$ within the unit cell and

$$x_1 \equiv x_{l_1 l_2 l_3} = l_1 a_1 + l_2 a_2 + l_3 a_3,$$

is the lattice translational vector of the $i$th unit cell and the vectors $a_j$ are called the primitive translational vectors of the lattice. In Eq. 1.2, $l_1, l_2, l_3$ are integers. With
this notation, we write \( \mathbf{R}''_k = \mathbf{R}''_k = x_{lk} + u_{lk} \), where \( lk \) go over \( N_n - 1 \) values in total. In the case of the quantities \( x_k \) and \( u_k \), we sometimes use the following collective notation \( x \equiv x_1, \ldots, x_{N_n-1} \) and \( u \equiv u_1, \ldots, u_{N_n-1} \).

We use the following shorthand notation for the position and time variables

\[
i \equiv r_i t_i, \quad (i-j) \equiv \delta (t_i - t_j) \delta (r_i - r_j),
\]

\[
v (1,2) = \delta (t_1 - t_2) v (r_1,r_2),
\]

\[
\int di = \int d\mathbf{r}_i \int dt_i.
\]

(A3)

In this work, we use the following convention for the Fourier transforms

\[
f (\omega) = \int_{-\infty}^{\infty} dt f (t) e^{i\omega t},
\]

\[
f (t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega f (\omega) e^{-i\omega t}.
\]

(A4)

Appendix B: Euler angles

The condition given by Eq. (13) defines the Euler angles by an implicit equation of the form \( \mathbf{F} (\theta, \mathbf{x} + \mathbf{u}) = 0 \). In general, no explicit solution of such equations exists, however. That is, it might not be possible to write \( \theta \) as an explicit function of the nuclei variables \( \mathbf{x}, \mathbf{u} \), but for a given \( \mathbf{x}, \mathbf{u} \) and the nuclei masses, a numerical solution could be sometimes obtained. We are in particular interested how to obtain the rotation matrix \( \mathcal{R} [\theta (\mathbf{x})] \) and its derivatives since these quantities appear in the Hamiltonian if we establish the Taylor expansions of some parts of the Hamiltonian (see Appendix D) and thus they will eventually appear in the EOM.

The rotation matrix \( \mathcal{R} [\theta (\mathbf{x} + \mathbf{u})] \) can be obtained from the generic conditions given by Eq. (13). In turn, \( \mathcal{R} [\theta (\mathbf{x})] \) can be obtained by solving Eq. (13) with \( \mathbf{u} = 0 \). Thus, \( \mathcal{R} [\theta (\mathbf{x})] \) is obtained from the implicit equation

\[
\mathbf{F} (\theta, \mathbf{x}) = 0.
\]

(B1)

For instance, in the case of Eckart conditions given by Eq. (14)

\[
\sum_{k=1}^{N_n-1} M_k \mathbf{x}_k \times \mathcal{R} (\theta) \mathbf{x}_k = 0,
\]

(B2) By the chain rule, we write

\[
\frac{\partial \mathcal{R}}{\partial x_\alpha} (k) = \sum_{\beta=1}^{3} \frac{\partial \mathcal{R}}{\partial \theta_\beta} \frac{\partial \theta_\beta}{\partial x_\alpha} (k),
\]

\[
\frac{\partial^2 \mathcal{R}}{\partial x_\beta} (k)\partial x_\alpha (k) = \sum_{\beta',\beta''=1}^{3} \frac{\partial^2 \mathcal{R}}{\partial \theta_{\beta'} \partial \theta_{\beta''}} \frac{\partial \theta_{\beta'}}{\partial x_\alpha} (k) \frac{\partial \theta_{\beta''}}{\partial x_\beta (k')} + \sum_{\beta'=1}^{3} \frac{\partial \mathcal{R}}{\partial \theta_{\beta'}} \frac{\partial^2 \theta_{\beta'}}{\partial x_\alpha (k) \partial x_\beta (k')}.
\]

(B3)

Given the explicit form for the rotation matrix as a function of the Euler angles we can calculate the derivatives like \( \partial \mathcal{R} / \partial \theta_\beta \), so next we find a way how to calculate the derivatives like \( \partial \theta_{\beta'} / \partial x_\alpha (k) \) and \( \partial^2 \theta_{\beta''} / \partial x_\alpha (k) \partial x_\beta (k') \). After taking the total derivative of \( F_\sigma (\theta, \mathbf{x}, \mathbf{u}) \) with respect to \( x_\alpha (k) \) we write

\[
\frac{dF_\sigma}{dx_\alpha (k)} = \sum_{\beta'=1}^{3} A_{\sigma \beta'} \frac{\partial \theta_{\beta'}}{\partial x_\alpha (k)} + \frac{\partial F_\sigma}{x_\alpha (k)} = 0,
\]

(B4)

where \( A_{\sigma \beta'} \equiv \partial F_\sigma / \partial \theta_{\beta'} \). Suppose that the matrix \( A \) is invertible such that

\[
\sum_{\sigma=1}^{3} A_{\gamma \sigma} A_{\sigma \beta'} = \delta_{\gamma \beta'}.
\]

(B5)

By multiplying Eq. (B4) with \( A_{\gamma \sigma}^{-1} \), taking a sum over \( \sigma \) and re-arranging, we obtain

\[
\frac{\partial \theta_{\gamma}}{\partial x_\alpha (k)} = - \sum_{\sigma=1}^{3} A_{\gamma \sigma}^{-1} \frac{\partial F_\sigma}{x_\alpha (k)}.
\]

(B6)

The result given by Eq. (B6) is essentially included to the implicit function theorem. For the second order derivative, we take the total derivative of Eq. (B6) with respect to \( x_\beta (k') \) and after some algebra find that

\[
\frac{\partial^2 \theta_{\gamma}}{dx_\alpha (k) \partial x_\beta (k')} = - \sum_{\sigma=1}^{3} A_{\gamma \sigma}^{-1} \frac{\partial^2 F_\sigma}{x_\alpha (k) \partial x_\beta (k')} + \sum_{\beta'', \sigma=1}^{3} A_{\gamma \sigma}^{-1} \frac{\partial \theta_{\beta''}}{\partial x_\alpha (k)} \frac{\partial^2 F_\sigma}{\partial \theta_{\beta''} \partial x_\beta (k')} + \sum_{\beta'=1}^{3} \frac{\partial \mathcal{R}}{\partial \theta_{\beta'}} \frac{\partial^2 \theta_{\beta'}}{\partial x_\alpha (k) \partial x_\beta (k')}.
\]

(B7)

All the quantities in Eqs. (B6) and (B7) are to be evaluated at \( \theta = \theta (\mathbf{x}), \mathbf{u} = 0 \) when applied in solving the relations of Eq. (B5) aiming to evaluate \( \mathcal{R} [\theta (\mathbf{x})] \). For instance, when the condition \( F_\sigma (\theta, \mathbf{x}, \mathbf{u}) \) is assumed to be
the Eckart condition given by Eq. [4] we have
\[ \frac{\partial F_\alpha}{\partial \theta^\beta} = \sum_{k=1}^{N_u} \frac{3}{M_k} \sum_{\eta,\nu=1}^{3} \epsilon_{\eta,\nu} x_\eta (k) \frac{\partial R_{\nu,\beta}^\gamma}{\partial \theta^\beta} R_{\nu,\beta}^\gamma (k), \]
\[ \frac{\partial F_\alpha}{\partial x_\alpha (k)} = M_k \sum_{\nu=1}^{3} \epsilon_{\sigma,\nu} \sum_{\beta=1}^{3} R_{\nu,\beta}^\gamma R_{\nu,\beta}^\gamma (k) \]
\[ + M_k \sum_{\eta,\nu=1}^{3} \epsilon_{\gamma,\nu} x_\eta (k) R_{\nu,\alpha}, \]
and so on. Here, \( \epsilon_{\sigma,\nu} \) is the Levi-Civita symbol.

**Appendix C: Coriolis and vibrational-rotational coupling terms**

The kinetic energy contributions \( \hat{T}_{\text{cuv}} \) and \( \hat{T}_{\text{cuv}}' \) are
\[ \hat{T}_{\text{cuv}} = \sum_{\beta,\gamma} \hat{T}_{\text{cuv}}^{(1)} (r) \frac{\partial \hat{\psi} (r)}{\partial r_\gamma} \]
\[ + \sum_{k=1}^{N_u} \sum_{\alpha,\gamma} \hat{T}_{\text{cuv}}^{(2)} (k) \hat{p}_\alpha (k) \]
\[ \times \int dr \hat{\psi}^\dagger (r) r_\gamma \frac{\partial \hat{\psi}^\dagger (r)}{\partial r_\beta}, \]
\[ \hat{T}_{\text{cuv}}' = \sum_{\sigma,\gamma} \hat{T}_{\text{cuv}}'^{(1)} (r) \frac{\partial \hat{\psi} (r)}{\partial r_\gamma} \]
\[ + \sum_{k=1}^{N_u} \sum_{\alpha,\gamma} \hat{T}_{\text{cuv}}'^{(2)} (k) \hat{p}_\alpha (k) \]
\[ \times \int dr \hat{\psi}^\dagger (r) r_\gamma \frac{\partial \hat{\psi}^\dagger (r)}{\partial r_\sigma}, \]
and
\[ \hat{M}_{\gamma \sigma} (k) = \frac{\hbar^2}{2M u_k} \sum_{k'=1}^{N_u} \sum_{\alpha,\sigma}^{3} \frac{\partial^2 \hat{R}_{\gamma \sigma} (k)}{\partial r_\alpha (k')} \hat{R}_{\gamma \sigma}^T (k'), \]
\[ \hat{M}_{\alpha \gamma} (k) = \frac{i \hbar}{M u_k} \sum_{k'=1}^{N_u} \sum_{\sigma=1}^{3} \frac{\partial \hat{R}_{\alpha \sigma} (k)}{\partial r_\gamma (k')} \hat{R}_{\gamma \sigma}^T (k'), \]
\[ \hat{M}_{\gamma \alpha} (k') = - \frac{\hbar^2}{2M u_k} \sum_{k''=1}^{N_u} \sum_{\sigma=1}^{3} \frac{\partial \hat{R}_{\gamma \sigma} (k)}{\partial r_\alpha (k'')} \hat{R}_{\gamma \sigma}^T (k''), \]
and
\[ \hat{M}_{\gamma \alpha} (k) = \frac{i \hbar}{M u_k} \sum_{k'=1}^{N_u} \sum_{\sigma=1}^{3} \frac{\partial \hat{R}_{\alpha \sigma} (k)}{\partial r_\gamma (k')} \hat{R}_{\gamma \sigma}^T (k'), \]
\[ \times \frac{\partial \hat{R}_{\gamma \sigma} (k)}{\partial r_\alpha (k)} \hat{R}_{\gamma \sigma}^T (k'), \]
\[ \hat{M}_{\alpha \gamma} (k) = \frac{i \hbar}{M u_k} \sum_{k'=1}^{N_u} \sum_{\sigma=1}^{3} \frac{\partial \hat{R}_{\alpha \sigma} (k)}{\partial r_\gamma (k')} \hat{T}_{\gamma \sigma}^T (k'), \]
\[ \hat{M}_{\gamma \alpha} (k') = - \frac{\hbar^2}{2M u_k} \sum_{k''=1}^{N_u} \sum_{\sigma=1}^{3} \frac{\partial \hat{R}_{\gamma \sigma} (k)}{\partial r_\alpha (k'')} \hat{R}_{\gamma \sigma}^T (k''), \]
\[ \times \frac{\partial \hat{R}_{\gamma \sigma} (k)}{\partial r_\alpha (k)} \hat{R}_{\gamma \sigma}^T (k''), \]
\[ \times \frac{\partial \hat{R}_{\gamma \sigma} (k)}{\partial r_\alpha (k)} \hat{R}_{\gamma \sigma}^T (k'). \]

Here we divided the Coriolis and vibrational-rotational coupling terms into two parts, the other part \( \hat{T}_{\text{cuv}}' \), is proportional to the inverse of the total nuclei mass while the other, \( \hat{T}_{\text{cuv}} \), is not. All the quantities defined by Eqs. [2] and [3] are functions of \( \mathbf{x} \) and \( \mathbf{u} \). Strictly speaking, the derivatives like \( \partial \hat{R}_{\sigma \sigma} / \partial u_\alpha (k') \), are not so well defined objects from a notational point of view. By this notation we mean that the quantities like \( \partial \hat{R}_{\sigma \sigma} / \partial u_\alpha (k') \) and \( \partial^2 \hat{R}_{\sigma \sigma} / \partial u_\alpha (k) \), are some functions of \( \mathbf{x} \), \( \mathbf{u} \) after differentiation and we can then find the corresponding functions of operators in the abstract space. For example if \( \partial \hat{R} / \partial u_\alpha (k) = G_\alpha (k, \mathbf{x}, \mathbf{u}) \), then in our notation \( \partial \hat{R} / \partial u_\alpha (k) = G_\alpha (k, \mathbf{x}, \mathbf{u}) \).

We also use the following form of the Coriolis and vibrational-rotational coupling terms
\[ \hat{T}_{\text{cuv}} + \hat{T}_{\text{cuv}}' = \sum_{c=1}^{3} \hat{T}_{\text{cuv}}^{(c)}, \]
where
\[ \hat{T}_{\text{cuv}}^{(1)} = \sum_{\beta,\gamma} \int dr \gamma \frac{\partial \hat{\psi}^\dagger (r)}{\partial r_\beta} \hat{\psi}^\dagger (r) \hat{\psi} (r), \]
\[ \hat{T}_{\text{cuv}}^{(2)} = \sum_{k=1}^{N_u} \int dr \gamma \frac{\partial \hat{\psi}^\dagger (r)}{\partial r_\beta} \hat{\psi} (r), \]
\[ \hat{T}_{\text{cuv}}^{(3)} = \sum_{k=1}^{N_u} \int dr \gamma \frac{\partial \hat{\psi}^\dagger (r)}{\partial r_\beta} \hat{\psi}^\dagger (r) \hat{\psi} (r) \hat{\psi} (r), \]
and the quantities \( \hat{\psi}^\dagger, \hat{\psi}^\dagger \), and \( \hat{\psi}^\dagger \) are defined by Eq. [2]

**Appendix D: Useful relations**

We expand \( \hat{\psi}^\dagger (r) \), \( \hat{V}_{\text{en}} (r) \) and \( \hat{V}_{\text{nn}}'' \) to Taylor series in displacements and write (see Appendix [A] for the nota-
We note that from these expansions it follows that

\[ \hat{V}_{nn} = \sum_{m=0}^{\infty} \frac{1}{m!} \sum_{k_m, o_m} \frac{\partial^m V_{nn}(x)}{\partial x_{o_m}(k_m)} \hat{u}_{o_m}(k_m), \]

\[ V_{nn}(x) = \sum_{k, k'=1}^N v(x_k, x_{k'}), \]

\[ x_{N_n} = -\frac{1}{MN_n} \sum_{k=1}^{N_n-1} M_k x_k, \]

\[ \hat{V}_{en}(r) = \sum_{m=0}^{\infty} \frac{1}{m!} \sum_{k_m, o_m} \frac{\partial^m V_{en}(r, x)}{\partial x_{o_m}(k_m)} \hat{u}_{o_m}(k_m), \]

\[ V_{en}(r, x) = \sum_{k=1}^{N_n} \frac{-Z_k}{|r - \mathcal{R}[\theta(x)] x_k|}, \quad (D1) \]

and

\[ \hat{n}_n(r) = \sum_{m=0}^{\infty} \frac{1}{m!} \sum_{k_m, o_m} \frac{\partial^m n_{n}^{(0)}(x, r)}{\partial x_{o_m}(k_m)} \hat{u}_{o_m}(k_m), \]

\[ n_{n}^{(0)}(x, r) \equiv -\sum_{k=1}^{N_n} Z_k \delta(r - \mathcal{R}[\theta(x)] x_k). \quad (D2) \]

In Appendix B we discuss how to actually obtain the rotation matrix \( \mathcal{R}[\theta(x)] \) and the necessary derivatives of it.

Next we set out to derive an exact form of the total energy of the system. We start by writing

\[ \hat{V}_{nn} = \sum_{m=0}^{\infty} \hat{V}_{mn}^{(m)}, \quad \hat{V}_{en}(r) = \sum_{m=0}^{\infty} \hat{V}_{en}^{(m)}(r), \quad (D3) \]

where

\[ \hat{V}_{mn}^{(m)} = \frac{1}{m!} \sum_{k_m, o_m} \frac{\partial^m V_{nn}(x)}{\partial x_{o_m}(k_m)} \hat{u}_{o_m}(k_m), \]

\[ \hat{V}_{en}^{(m)} = \frac{1}{m!} \sum_{k_m, o_m} \frac{\partial^m V_{en}(r, x)}{\partial x_{o_m}(k_m)} \hat{u}_{o_m}(k_m), \quad (D4) \]

such that

\[ \hat{V}_{nn} = \int dr \sum_{m=0}^{\infty} \hat{V}_{en}^{(m)}(r) \hat{n}_e(r). \quad (D5) \]

We note that from these expansions it follows that

\[ \langle \hat{V}_{en}^{(m)} \rangle = -\frac{1}{ih} \int dr V_{en}(r, x) G(rt, rt^+) \]

\[ -\frac{1}{ih} \sum_{m=1}^{\infty} \frac{1}{m} \sum_{k, o} \int dr \langle \hat{p}_o(k) \hat{V}_{en}^{(m)}(r) \rangle \hat{u}_o(k) \hat{n}_e(r), \quad (D6) \]

and

\[ \langle \hat{V}_{nn}^{(m)} \rangle = V_{nn}(x) - \frac{1}{ih} \sum_{m=1}^{\infty} \frac{1}{m} \sum_{k, o} \int dr \langle \hat{p}_o(k) \hat{V}_{en}^{(m)}(r) \rangle \hat{u}_o(k) \hat{n}_e(r), \quad (D7) \]

where we used \( \langle \hat{n}_e(rt) \rangle = -\frac{i}{\hbar} G(rt, rt^+). \) We write the quantity defined by Eq. (D7) as \( K_{\alpha}^n(kt) = K_{\alpha}^{en}(kt) + K_{\alpha}^{nn}(kt) \) such that

\[ K_{\alpha}^n(kt) = \frac{1}{i\hbar} \langle \hat{p}_o(k) \hat{V}_{nn}^{(m)} \hat{u}_o(k) \rangle, \quad (D8) \]

where \( y = en, nm. \) In a similar way we write the quantity defined by Eq. (D9) as \( K_{\alpha}^{nn}(kt, k't') = K_{\alpha}^{nn}(kt, k't') + K_{\alpha}^{nn}(kt, k't') \), where

\[ K_{\alpha}^{nn}(kt, k't') = \frac{\delta K_{\alpha}^n(kt)}{\delta j_{\beta}(k't')} \quad (D9) \]

We define

\[ \Pi_{\alpha\alpha'}(kt, k't) \equiv -\sum_{k', \beta} \int dt' K_{\alpha\beta}^n(kt, k't') D_{\beta\alpha'}^{-1}(k't', k'), \quad (D10) \]

Next we use Eq. (D3) and write \( K_{\alpha}^{en}(kt) \) and \( K_{\alpha}^{nn}(kt) \) such that

\[ K_{\alpha}^n(kt) = \sum_{m=1}^{\infty} K_{\alpha}^{en}(m)(kt), \quad (D11) \]

and in a similar way for all the quantities derived by using \( K_{\alpha}^{nn}(kt) \) and \( K_{\alpha}^{nn}(kt) \). By using Eq. (D11) in Eqs. (D9) and (D10) and these results with Eqs. (D6) and (D7) we eventually find that

\[ \langle \hat{V}_{en}^{(m)} \rangle = V_{en}(x) - \frac{1}{ih} \sum_{m=1}^{\infty} \frac{1}{m} \sum_{k, o} K_{\alpha}^{en,m}(kt) \langle \hat{u}_o(k) \rangle \]

\[ + \frac{i}{h} \sum_{m=1}^{\infty} \frac{1}{m} \sum_{k, o, k', o'} \int dr'' T_{\alpha\alpha'}^{en,m}(kt, k''t'') \]

\[ \times D_{\alpha'\alpha}(k''t'', kt), \quad (D12) \]

and

\[ \langle \hat{V}_{nn}^{(m)} \rangle = -ih \int dr V_{en}(r, x) G(rt, rt^+) \]

\[ - \sum_{m=1}^{\infty} \frac{1}{m} \sum_{k, o} K_{\alpha}^{en,m}(kt) \langle \hat{u}_o(k) \rangle \]

\[ + \frac{i}{h} \sum_{m=1}^{\infty} \frac{1}{m} \sum_{k, o, k', o'} \int dr'' T_{\alpha\alpha'}^{en,m}(kt, k''t'') \]

\[ \times D_{\alpha'\alpha}(k''t'', kt). \quad (D13) \]

We use these results to write the total energy \( E_{tot} \) in terms of the Green’s functions and related quantities. We write

\[ E_{tot} = \langle \hat{T}_{tot} \rangle + \langle \hat{V}_{ee}^{(m)} \rangle + \langle \hat{V}_{en}^{(m)} \rangle + \langle \hat{V}_{nn}^{(m)} \rangle, \quad (D14) \]
where the external potentials are put to zero and $\hat{T}_{tot}$ is given by Eq. 17. We have

$$\langle \hat{T}^\alpha \rangle = \frac{-i\hbar}{2M_{en}} \int dr \nabla^2_r G (r, rt^+) ,$$

$$\langle \hat{T}^\alpha \rangle = \frac{i\hbar}{2M_{en}} \int \sum_{k=1}^{N-1} \sum_{\alpha=1}^{3} \frac{M_{en}}{M_{en}} D^{pp,T}_{\alpha\beta} (kt, kt^+) ,$$

$$\langle \hat{T}_{\alpha\beta} \rangle = -\frac{i\hbar}{2M_{en}} \int \sum_{k=1}^{N-1} \sum_{\alpha=1}^{3} D^{pp,T}_{\alpha\beta} (kt, kt^+) .$$

(D15)

Here

$$D^{pp,T}_{\alpha\beta} (kt, kt^+) \equiv \frac{1}{i\hbar} \langle \hat{T} \{ \hat{p}_{\alpha} (kt) \hat{p}_{\beta} (kt^+) \} \rangle ,$$

(D16)

and this function can be obtained from the solution of Eq. 55 since with the external potentials put to zero $\langle \hat{p}_{\alpha} (kt) \rangle = \langle \hat{p}_{\alpha} (k) \rangle$. By using the EOM for the field operator given by Eq. 26 without the external potentials we find that

$$\langle \hat{T}^\alpha \rangle = \frac{i\hbar}{2} \int dr \left[ -i\hbar \frac{\partial}{\partial t} - \frac{\hbar^2}{2m_e} \nabla^2_r \right] G (r, rt^+)$$

$$= \frac{1}{2} \left[ \langle \hat{T}^{(1)} \rangle + \langle \hat{T}^{(2)} \rangle \right] \right]$$

$$+ \langle \hat{T}^{(3)} \rangle$$

$$+ \langle \hat{T}^{(4)} \rangle + \langle \hat{T}^{(5)} \rangle$$

(D17)

where $\hat{T}^{(i)}$ are given by Eqs. 34 and 35. This result can be found by multiplying Eq. 26 from the left with $\hat{\psi}^\dagger (rt^+) r / 2$, integrating over $r$, taking an ensemble average and then establishing some rearranging. From Eqs. 38 and from Eqs. 35 and 33 of Appendix B it follows that

$$\langle \hat{T}^{(1)} \rangle + \langle \hat{T}^{(2)} \rangle = -i\hbar \int d\tau \int d\tau^\prime \int dt^\prime \Sigma_2 (r, \tau^\prime)$$

$$\times G (r^\prime, \tau^\prime, \tau) .$$

(D18)

By using Eqs. 12, 13, 17, and 18 the total energy can be written as

$$E_{tot} = \frac{i\hbar}{2} \sum_{k,k'=1}^{N-3} \sum_{\alpha=1}^{3} (M_{k-1}^{\alpha\beta} - M_{nuc}^{\alpha\beta}) D^{pp,T}_{\alpha\beta} (kt, kt^+)$$

$$- \frac{i\hbar}{2} \sum_{m=1}^{1} \sum_{k,\alpha}^{N-3} K_{\alpha}^{nn,(m)} (kt) + 2K_{\alpha}^{nn,(m)} (kt) \langle \hat{u}_{\alpha} (kt) \rangle$$

$$+ V_{nn} (x) + \frac{i\hbar}{2} \sum_{m=1}^{1} \sum_{k,\alpha}^{N-3} \sum_{k',\alpha'}^{N-3} \int dt''$$

$$\times \left[ \Pi_{\alpha\alpha'}^{nn,(m)} (kt, kt''^+) + 2 \Pi_{\alpha\alpha'}^{nn,(m)} (kt, kt''^+) \right]$$

$$\times D_{\alpha\alpha} (k''^+, kt)$$

$$- \frac{i\hbar}{2} \int d\tau \left[ \frac{\hbar^2}{2m} \nabla^2_r + V_{en} (r, x) \right] G (r, rt^+)$$

$$- \frac{i\hbar}{2} \int d\tau \int d\tau^\prime \int dt^\prime \Sigma_2 (r, \tau^\prime, \tau) G (r^\prime, \tau^\prime, \tau) .$$

(D19)

This is an exact form of $E_{tot}$. Provided $x$ are the equilibrium positions, then the second term on the right hand side of Eq. 119 involving $\langle \hat{u}_{\alpha} (kt) \rangle$ vanishes and $D_{\alpha\alpha} (k''^+, kt) = D_{\alpha\alpha} (k''^+, kt^+)$. 

ACKNOWLEDGMENTS

V. J. H. thanks Dr. Ivan Gonoskov for useful discussions on various aspects of the present work.

1. M. Born and R. Oppenheimer, Ann. Phys. (Leipzig) 389, 457 (1927).
2. K. Huang and M. Born, Dynamical Theory of Crystal Lattices (Clarendon Press Oxford, 1954).
3. P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
4. W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
5. R. G. Parr and W. Yang, Density Functional Theory of Atoms and Molecules (Oxford University Press, 1989).
6. R. M. Dreizler and E. K. U. Gross, Density Functional Theory: An Approach to the Quantum Many-Body Problem (Springer-Verlag, 1990).
7. P. C. Martin and J. Schwinger, Phys. Rev. 115, 1342 (1959).
8. G. Baym, Ann. Phys. 14, 1 (1961).
9. E. G. Maksimov, Zh. Eksp. Teor. Fiz 69, 2236 (1975).
10. L. Hedin, Phys. Rev. 139, A796 (1965).
11. G. Mahan, Many-Particle Physics (Plenum Press, 1990).
12. A. Fetter and J. Walecka, Quantum Theory of Many-Particle Systems (McGraw-Hill, 1971).
13. G. Stefanucci and R. van Leeuwen, Nonequilibrium Many-Body Theory of Quantum Systems (Cambridge University Press, 2013).
14. A. A. Maradudin and A. E. Fein, Phys. Rev. 128, 2589 (1962).
15. R. A. Cowley, Adv. Phys. 12, 421 (1963).
16. R. Shukla and E. Cowley, Phys. Rev. B 3, 4055 (1971).
17. G. Rickayzen, Green’s Functions and Condensed Matter, Acad (Academic Press, 1980).
18. A. A. Maradudin, Elements of The Theory of Lattice Dynamics, Vol. 1 (North-Holland Publishing Company, 1974) pp. 1–82.
19. P. Giannoni, S. de Gironcoli, P. Pavone, and S. Baroni, Phys. Rev. B 43, 7231 (1991).
20. S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannoni, Rev. Mod. Phys. 73, 515 (2001).
