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Quantum chemical study of electron-phonon interaction in crystals

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Study of the interaction of the electromagnetic radiation with nonlocal potentials and the electron-phonon interaction is motivated by its key role in non-classical phenomena in dielectrics and semiconductors. Actual in second quantization is decoupling of the undesirable mixture of electronic and phonon birth/annihilation operators and obtaining the effect of radiation in presence of the nonlocal potentials. Here we transform an arbitrary effective electron- phonon Hamiltonian in two matrices – the matrix of a new interaction Hamiltonian and the matrix of the transformation. For a particular effective Hamiltonian formulated in second quantization these two matrices outline a starting point to decouple the electron-phonon interaction by transformation of the lattice Hamiltonian to a purely electronic one available for wave function and atomic orbital approaches. The impact of external electromagnetic radiation is incorporated through the birth/annihilation operators.

1 Introduction First-principles calculations of the interaction of quantum systems with electromagnetic radiation is a long standing and practically important problem to the electronic structure of dielectrics and semiconductors with charge carriers and lattice deformations as the key factors in the formation of quasiparticles constituted of electrons dressed in a phonon cloud.

In early works this problem is determined by the type of particle-phonon interaction as implemented in Frölich [1, 2] and Holstein's [3, 4] models for optical phonons with polar long-range interaction and nonpolar short-range electron-phonon interaction, correspondingly.

In modern approaches [5] the effect of electromagnetic radiation and electron-phonon interaction is considered on equal terms of the lattice dynamics applicable to all types of interactions and plays a crucial role in describing conducting polymers, ferroelectrics, and several important classes of perovskites. Especially the research on high-T_c superconductivity and colossal magneto-resistance has spurred intense research to determine the leading role of these two fundamental interactions.

Objective of the present paper is a regular first-principles application to the conventional lattice models [6] supplemented with electromagnetic radiation [8] and electron–phonon interaction terms.

We present the transformation of an arbitrary effective electron-phonon Hamiltonian in two matrices - the matrix of a new interaction Hamiltonian and the matrix of the transformation. For a particular electron-phonon Hamiltonian these two matrices outline a starting point to decouple the electron-phonon interaction and transform the lattice Hamiltonian to a purely electronic one available for wave function and atomic orbital approaches. This last stage is quantum system specific and is out of scope of this work.

Content of the article comprises Section 2, where we discuss in detail the impact of electromagnetic radiation in case of effective Hamiltonians with nonlocal potentials. In Section 3 we treat the undesirable mixture of electronic and phonon birth/annihilation operators in arbitrary electron-phonon Hamiltonian by Baker-Hausdorf transformation. Section 4 shows implementation of electron-phonon interaction in Hartree-Fock method. Finally, concluding remarks are given Section 5.

2 Electromagnetic radiation Systems described by many-body Hamiltonians

$$H_0 = \sum_i \frac{p_i^2}{2m} + \sum_i V(\boldsymbol{x}_i, \boldsymbol{p}_i) \tag{1}$$

are distinguished by the nature of its potential energy. If the potential energy terms are local, the interaction with externally applied electromagnetic radiation contributes exclusively in the kinetic energy as described in the electric dipole approximation [7]. Nonlocal potentials appear when the many-body Hamiltonians are reduced (for computing convenience) to the effective Hamiltonians. The guiding idea in developing the interaction with nonlocal potentials $V(\boldsymbol{x})$ [8-10] leads to the electromagnetic radiation contributing to both the kinetic and the potential part as

$$H = \frac{1}{2m}\sum_i \left(\boldsymbol{p}_i - \frac{\boldsymbol{A}(\boldsymbol{x}_i)q}{c} \right)^2 + \sum_i V\left(\boldsymbol{x}, \left(\boldsymbol{p}_i - \frac{\boldsymbol{A}(\boldsymbol{x}_i)q}{c} \right) \right) \quad (2)$$

where $\boldsymbol{A}$ is the vector potential and $q = -|e|$.

In second quantization, dictated by the electron-phonon interaction and pioneered in [8-10], it is convenient to define a function $\chi(\boldsymbol{x})$ such that

$$\frac{\partial \chi(\boldsymbol{x}_i)}{\partial \boldsymbol{x}_i} = \hbar \boldsymbol{A}(\boldsymbol{x}_i) \quad (3)$$

Assuming that the interaction of particles with the magnetic field is minimal one can formally implement unitary transformation to the unperturbed Hamiltonian Eq. (1) as $H = UH_0U^{-1}$.

The unitary operator U

$$U(\boldsymbol{x}) = \exp\left[\frac{iq}{c\hbar} \sum_i \chi(\boldsymbol{x}_i) \right] \quad (4)$$

implicitly depends on the vector potential and transforms Hamiltonian H_0 into

$$H(\boldsymbol{x}) = \exp\left[\frac{iq}{c\hbar} \chi(\boldsymbol{x}) \right] H_0 \exp\left[\frac{-iq}{c\hbar} \chi(\boldsymbol{x}) \right]. \quad (5)$$

The relation [9] for two noncommuting operators f and g

$$e^{if(\boldsymbol{x})} g(\boldsymbol{x}, \boldsymbol{p}) e^{-if(\boldsymbol{x})} = g\left(\boldsymbol{x}, \boldsymbol{p} - \frac{\partial f(\boldsymbol{x})}{\partial \boldsymbol{x}} \right) \quad (6)$$

leads to

$$H = \sum_i H_0\left(\boldsymbol{x}_i, \boldsymbol{p}_i - \frac{q}{c\hbar} \frac{\partial \chi(\boldsymbol{x}_i)}{\partial \boldsymbol{x}_i} \right) = \sum_i H_0\left(\boldsymbol{x}_i, \boldsymbol{p}_i - \frac{q}{c} \boldsymbol{A} \right) \quad (7)$$

where matrix Eq. (4) accounts for the vector potential and is appropriate for second quantization. In Eq. (6) the generator of the canonical transformation $f(\boldsymbol{x}) = q / c\hbar \sum_i \chi(\boldsymbol{x}_i)$ and $g(\boldsymbol{x}, \boldsymbol{p}) \equiv H_0$.

In second quantization the Hamiltonian Eq. (1) reads as

$$H_0 = \int \Psi^+(\boldsymbol{x}) \left(\frac{p^2}{2m} + V(\boldsymbol{x}, \boldsymbol{p}) \right) \Psi(\boldsymbol{x}) d\boldsymbol{x} \quad (8)$$

where the field operators $\Psi^+(\boldsymbol{x}), \Psi(\boldsymbol{x})$, satisfying the boson or fermion commutation rules, are expanded in the eigenfunctions of the H_0 Eq. (1)

$$\Psi(\boldsymbol{x}) = \sum_n c_n \varphi_n(\boldsymbol{x}) \quad (9)$$

$$\Psi^+(\boldsymbol{x}) = \sum_n c_n^+ \varphi_n^+(\boldsymbol{x}) \quad (10)$$

where c^+ and c are birth and annihilation operators, respectively. In these terms the Hamiltonian Eq. (7) takes the form

$$H = \sum_{m',n'} c_{m'}^+ c_{n'} \langle \varphi_{m'} | U H_0 U^{-1} | \varphi_n \rangle. \quad (11)$$

Introducing the complete set of states $|\varphi_m\rangle$ the Eq. (11) yields

$$H = \sum_{m,n} \langle \varphi_m | H_0 | \varphi_n \rangle \left\{ \sum_{m'} \langle \varphi_{m'} | U | \varphi_m \rangle c_{m'}^+ \right\} \left\{ \sum_{n'} \langle \varphi_n | U^{-1} | \varphi_{n'} \rangle c_{n'} \right\} \quad (12)$$

According to Eq. (12), the Hamiltonian for a system interacting with electromagnetic radiation can be obtained in second quantized form directly from the unperturbed Hamiltonian replacing the annihilation and creation operators by the expressions in curled brackets of Eq. (12)

$$c_m \to \sum_n \langle \varphi_m | U^{-1} | \varphi_n \rangle c_n \quad (13)$$

$$c_m^+ \to \sum_n \langle \varphi_n | U | \varphi_m \rangle c_n^+ \quad (14)$$

Considering the Eq. (4), the interaction Hamiltonian may be found by expansion of the unitary operator in powers of $\chi(\boldsymbol{x}) = \sum_i \chi(\boldsymbol{x}_i)$

$$c_m \to c_m + \frac{iq}{c\hbar} \sum_n \left(\langle \varphi_m | \chi(\boldsymbol{x}) | \varphi_n \rangle c_n + \frac{1}{2} \left(\frac{iq}{c\hbar} \right)^2 \langle \varphi_m | \chi^2(\boldsymbol{x}) | \varphi_n \rangle c_n + \ldots \right) \quad (15)$$

$$c_m^+ \to c_m^+ - \frac{iq}{c\hbar} \times \sum_n \left(\langle \varphi_m | \chi(\boldsymbol{x}) | \varphi_n \rangle c_n^+ + \frac{1}{2} \left(\frac{iq}{c\hbar} \right)^2 \langle \varphi_m | \chi^2(\boldsymbol{x}) | \varphi_n \rangle c_n^+ + \ldots \right) \quad (16)$$

Replacement rules Eqs. (16), (17) apply for representation the complete problem in second quantization.

3 Electron-phonon interaction The approach starts with total electron-phonon Hamiltonian, $\boldsymbol{H}$, as sum of nonperturbed, $\boldsymbol{H}_0$, and perturbed, $\boldsymbol{H}_1$, parts

$$\boldsymbol{H} = \boldsymbol{H}_0 + \boldsymbol{H}_1 \tag{17}$$

given in second quantization form. Irrespective to a particular nature of interactions the nonperturbed Hamiltonian $\boldsymbol{H}_0$ comprises electron and phonon operators implemented in separate terms whereas the perturbed Hamiltonian $\boldsymbol{H}_1$ comprises a mixture of these operators due the electron-phonon coupling.

To focus on the electron subsystem we decouple the electron-phonon interaction by means of Baker - Hausdorf transformation

$$\tilde{\boldsymbol{H}} = e^{-S}\boldsymbol{H}e^{S} = \boldsymbol{H} + [\boldsymbol{H}, S] + \frac{1}{2}[[\boldsymbol{H}, S], S] \tag{18}$$

where $S^{+} = -S$ is the generator of the canonical transformation. Appropriate choice for the generator S is central in problems of coupling between electronic and vibrational degrees of freedom. In case specific approaches the generator is developed for e.g. Lang-Firsov transformation [11] to the Holstein Hamiltonian with purely local coupling, in Schriefer–Wolf transformation [12], and for quantum spin lattices with short-range interactions [13].

In turn, here we develop a general scenario for the canonical transformation generator, *S*, applicable for a broad class of systems with electron-phonon interaction.

By inserting Eq. (17) in Eq. (18) the first two terms reads as

$$\begin{aligned}\boldsymbol{H} + [\boldsymbol{H}, S] &= \boldsymbol{H}_0 + \boldsymbol{H}_1 + (\boldsymbol{H}_0 + \boldsymbol{H}_1) \\ &\times S - S(\boldsymbol{H}_0 + \boldsymbol{H}_1) = \boldsymbol{H}_0 + [\boldsymbol{H}_1, S]\end{aligned} \tag{19}$$

and eliminating the linear electron-phonon interaction by

$$\boldsymbol{H}_1 + [\boldsymbol{H}_0, S] = 0 \tag{20}$$

for the last terms we obtain

$$\frac{1}{2}[[\boldsymbol{H}, S], S] = -\frac{1}{2}[\boldsymbol{H}_1, S] \tag{21}$$

Inserting relations Eq. (19) and Eq. (21) in Eq. (18) redefines the $\boldsymbol{H}_1$ term of Hamiltonian Eq. (17) (comprising a mixture of symmetric and antisymmetric creation and annihilation operators) that in Eq. (17) is eliminated by canonical transformation $\boldsymbol{H}_{\text{int}}$

$$\tilde{\boldsymbol{H}} = \boldsymbol{H}_0 + \frac{1}{2}[\boldsymbol{H}_1, S] = \boldsymbol{H}_0 + \boldsymbol{H}_{\text{int}}. \tag{22}$$

The Hamiltonian $\tilde{\boldsymbol{H}}$ now contains two new entities - the generator of transformation, S, and $\boldsymbol{H}_{\text{int}}$.

Next we calculate the matrix elements of $\langle S\rangle, \langle \boldsymbol{H}_1\rangle$, in the basis of eigenfunctions of nonperturbed Hamiltonian $\boldsymbol{H}_0$

$$\boldsymbol{H}_0 |n\rangle = E_n |n\rangle \tag{23}$$

Matrix elements of the generator $\langle S\rangle$ are obtained using Eq. (20) and Eq. (23)

$$\begin{aligned}&\langle m|\boldsymbol{H}_1|n\rangle + \langle m|[\boldsymbol{H}_0, S]|n\rangle = \\ &\langle m|\boldsymbol{H}_1|n\rangle + \langle m|\boldsymbol{H}_0 S|n\rangle - \langle m|S\boldsymbol{H}_0|n\rangle = 0\end{aligned} \tag{24}$$

Second and third term of Eq. (24) yields $E_m^{*}\langle m|S|n\rangle$ and $E_n^{*}\langle m|S|n\rangle$, correspondingly. As a result

$$\langle m|\boldsymbol{H}_1|n\rangle + \left(E_m^{*} - E_n\right)\langle m|S|n\rangle = 0 \tag{25}$$

Rearranging the terms in Eq. (25) gives the matrix elements

$$\langle m|S|n\rangle = \frac{\langle m|\boldsymbol{H}_1|n\rangle}{\left(E_n - E_m^{*}\right)} \tag{26}$$

Similarly, calculation of matrix elements of the electron-phonon interaction $\boldsymbol{H}_{\text{int}}$ starts with matrix elements of Eq. (22)

$$\langle m|\boldsymbol{H}_{\text{int}}|n\rangle = \frac{1}{2}\{\langle m|\boldsymbol{H}_1 S|n\rangle - \langle m|S\boldsymbol{H}_1|n\rangle\} = \frac{1}{2}(a+b) \tag{27}$$

Here

$$a = \sum_g \langle m|\boldsymbol{H}_1|g\rangle\langle g|S|n\rangle = \sum_g \langle m|\boldsymbol{H}_1|g\rangle \frac{\langle g|\boldsymbol{H}_1|n\rangle}{E_n - E_g} \tag{28}$$

$$b = -\sum_g \langle m|S|g\rangle\langle g|\boldsymbol{H}_1|n\rangle = \sum_g \frac{\langle m|\boldsymbol{H}_1|g\rangle}{E_g - E_m}\langle g|\boldsymbol{H}_1|n\rangle \tag{29}$$

As a result, Eq. (27) reads

$$\langle m|\boldsymbol{H}_{\text{int}}|n\rangle = \frac{1}{2}\sum_g \langle m|\boldsymbol{H}_1|g\rangle\langle g|\boldsymbol{H}_1|n\rangle\left(\frac{1}{E_n - E_g} + \frac{1}{E_m - E_g}\right) \tag{30}$$

Matrix elements Eqs. (26), (30) are correct in the absence of linear terms of $\boldsymbol{H}_1$ in $\tilde{\boldsymbol{H}}$ and constitutes a background for calculations of the operator $\boldsymbol{H}_{\text{int}}$ for a particular electron-phonon system. Complete electronic Hamiltonian has the form of Eq. (22) and include representation of the real space lattice Hamiltonian in the second quantization form and with birth and annihilation operators corrected by Eqs. (15), (16).

4 Electron-phonon interaction in the Hartree-Fock method It is temptative to implement the electron-phonon interaction in the Hartrtree-Fock method. In its conventional form this metod [6] assumes an electronic Hamiltonian in coordinate space comprising kinetic, electron-ion, ion-ion, and electron-electron energy terms, as well as the true ground state wave function, Ψ, that can be approximed by single-particle states, ψ, associated with

atomic orbitals obeying symmetry/antisymmetry conditions

$$\Psi(\boldsymbol{x}_1,...,\boldsymbol{x}_A)=\psi_{k_1}(\boldsymbol{x}_1)...\psi_{k_A}(\boldsymbol{x}_A) \tag{31}$$

$$H\Psi = E\Psi \tag{32}$$

$$E=\sum_{k}^{A}\varepsilon_k \tag{33}$$

Here E is energy that can be minimized at appropriate choice of single-particle states, ψ . In the second quantization approach it is convenient to categorize the electronic Hamiltonian in one-body operators $f(\boldsymbol{x}_k)$ that depend only on the coordinates of a single-particle, for example the kinetic energy , and two-body operators that involve coordinates of two particles, such as an interaction potential. As a result, in second quantization the problem is readdressed to one-body and two-body operators. One-body operators such as the kinetic energy and the electron- ion potential energy

$$\hat{f}=\sum_{jj'}f_{jj'}\hat{a}_j^{+}\hat{a}_{j'} \tag{34}$$

(with single-particle matrix elements $f_{jj'}$ defined by the single-particle wave functions) and two-body operators such as the electron-electron potential energy

$$\hat{V}=\frac{1}{2}\sum_{ijkl}v_{ijkl}\hat{a}_i^{+}\hat{a}_j^{+}\hat{a}_l\hat{a}_k \tag{35}$$

with the two-particle matrix element defined by the single-particle wave functions $\psi(\boldsymbol{x})$.
General form of the Hamiltonian is given by

$$\hat{H}=\sum_{ij}v_{ij}\hat{a}_i^{+}\hat{a}_i+\frac{1}{2}\sum_{ijkl}v_{ijkl}\hat{a}_i^{+}\hat{a}_j^{+}\hat{a}_l\hat{a}_k \tag{36}$$

in the sense that the expectation value of energy has a minimum at the ground state achieved as a solution of matrix equation for v_{ij} and v_{ijkl} . Reasonable implementation of the electron – phonon part from the Eq. (23) in the Hartree-Fock method is to add $\boldsymbol{H}_1$ to the Eq. (36) as a two-body operator.

5 Concluding remarks We suggest a regular first-principles treatment of quantum lattice systems distinguished by electron-phonon interaction and interaction with external electromagnetic radiation.

The treatment is based on the Baker-Hausdorf transformation of arbitrary interaction Hamiltonian and yields two matrices both of the generator of this transformation and of the transformed electron-phonon interaction. These two matrices suggest a starting point for a particular lattice Hamiltonian to decouple the electron-phonon interaction by transformation of a particular lattice Hamiltonian to a purely electronic one. The impact of electromagnetic radiation is incorporated through the birth and annihilation operators. As a result, this treatment condenses all key ingredients of a quantum lattice system and fits with the Hartree-Fock method in the second quantization form as advancement.

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