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Introduction

1.1 First-Principle Hamiltonian

Charge carriers in inorganic and organic matter interact with ion vibrations. The corresponding electron–phonon interaction (EPI) dominates transport and other properties of many poor metals and semiconductors. EPI causes also phase transformations, including superconductivity. When EPI is sufficiently strong, electron Bloch states are affected even in the normal phase. Phonons are also affected by conduction electrons. In doped insulators, including the advanced materials discussed in this review, *bare* phonons are well defined in insulating parent compounds, but microscopic separation of electrons and phonons is not so straightforward in metals and heavily doped insulators [1], where the Born and Oppenheimer [2] and density functional [3,4] methods are used. Here, we have to start with the first-principle Hamiltonian describing conduction electrons and ions coupled by the Coulomb forces:

$$H = -\sum_i \frac{\nabla_i^2}{2m_\mathrm{e}} + \frac{e^2}{2}\sum_{i\neq i'} \frac{1}{|\mathbf{r}_i - \mathbf{r}_{i'}|} - Ze^2 \sum_{ij} \frac{1}{|\mathbf{r}_i - \mathbf{R}_j|} + \frac{Z^2e^2}{2}\sum_{j\neq j'} \frac{1}{|\mathbf{R}_j - \mathbf{R}_{j'}|} - \sum_j \frac{\nabla_j^2}{2M}, \tag{1.1}$$

where $\mathbf{r}_i, \mathbf{R}_j$ are the electron and ion coordinates, respectively, $i = 1, \ldots, N_\mathrm{e}$; $j = 1, \ldots, N$; $\nabla_i = \partial/\partial\mathbf{r}_i$, $\nabla_j = \partial/\partial\mathbf{R}_j$, Ze is the ion charge, and M is the ion mass. The system is neutral, $N_\mathrm{e} = ZN$. The inner electrons are strongly coupled to the nuclei and follow their motion, so the ions can be considered as rigid charges. To account for their "high-energy" electron degrees of freedom, we can replace the elementary charge in (1.1) by $e/\sqrt{\epsilon}$, where ϵ is the high-frequency dielectric constant, or introduce an electron–ion "pseudopotential" [5] instead of the bare Coulomb electron–nuclear interaction.

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1.2 Local Density Approximation

One cannot solve the corresponding Schrödinger equation perturbatively because the Coulomb interaction is strong. The ratio of the characteristic Coulomb energy to the kinetic energy is $r_\mathrm{s} = m_\mathrm{e} e^2/(4\pi n_\mathrm{e}/3)^{1/3} \approx 1$ for the electron density $n_\mathrm{e} = ZN = 10^{23}\,\mathrm{cm}^{-3}$ (here and further, we take the volume of the system as $V = 1$, unless specified otherwise, and $\hbar = c = k_\mathrm{B} = 1$). However, one can take advantage of the small value of the adiabatic ratio $m_\mathrm{e}/M < 10^{-3}$. Ions are heavy and the amplitudes of their vibrations, $\langle|\mathbf{u}|\rangle \simeq \sqrt{1/M\omega_\mathrm{D}}$, near equilibrium positions $\mathbf{R}_0 \equiv \mathbf{l}$ are much smaller than the lattice constant $a = N^{-1/3}$:

$$\frac{\langle|\mathbf{u}|\rangle}{a} \approx \left(\frac{m_\mathrm{e}}{M r_\mathrm{s}}\right)^{1/4} \ll 1. \tag{1.2}$$

In this estimate, we take the characteristic vibration frequency ω_D of the order of the ion plasma frequency $\omega_0 = \sqrt{4\pi N Z^2 e^2/M}$. Hence, one can expand the Hamiltonian in powers of $|\mathbf{u}|$.

Any further progress requires a simplifying physical idea, which commonly is to approach the ground state of the many-electron system via a one-electron picture. In the framework of the local density approximation (LDA), the Coulomb electron–electron interaction is replaced by an effective one-body potential $\mathcal{V}(\mathbf{r})$:

$$\mathcal{V}(\mathbf{r}) = -Ze^2 \sum_j \frac{1}{|\mathbf{r} - \mathbf{R}_j|} + e^2 \int \mathrm{d}\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \mu_\mathrm{ex}[n(\mathbf{r})], \tag{1.3}$$

where $\mu_\mathrm{ex}[n(\mathbf{r})]$ is the exchange interaction, usually calculated numerically or expressed as $\mu_\mathrm{ex}[n(\mathbf{r})] = -\beta n(\mathbf{r})^{1/3}$ with a constant β in the simplest approximation. Here, $\mathcal{V}(\mathbf{r})$ is a functional of the electron density $n(\mathbf{r}) = \sum_s \langle \Psi_s^\dagger(\mathbf{r}) \Psi_s(\mathbf{r})\rangle$, where $\Psi_s(\mathbf{r})$ annihilates the electron with spin s and coordinate $\mathbf{r}$. As a result, in second quantization for electrons the Hamiltonian takes the form

$$H = H_\mathrm{e} + H_\mathrm{ph} + H_\mathrm{e\text{–}ph} + H_\mathrm{e\text{–}e}, \tag{1.4}$$

where

$$H_\mathrm{e} = \sum_s \int \mathrm{d}\mathbf{r} \Psi_s^\dagger(\mathbf{r}) \left[-\frac{\nabla^2}{2m_\mathrm{e}} + V(\mathbf{r})\right] \Psi_s(\mathbf{r}) \tag{1.5}$$

is the electron energy in a periodic crystal field $V(\mathbf{r}) = \sum_\mathbf{l} v(\mathbf{r} - \mathbf{l})$, which is $\mathcal{V}(\mathbf{r})$ calculated at $\mathbf{R}_j = \mathbf{l}$ with the periodic electron density $n^{(0)}(\mathbf{r} + \mathbf{l}) = n^{(0)}(\mathbf{r})$:

$$H_\mathrm{ph} = \sum_\mathbf{l} \left[-\frac{\nabla_\mathbf{u}^2}{2M} + \mathbf{u}_\mathbf{l} \cdot \frac{\partial}{\partial \mathbf{l}} \int \mathrm{d}\mathbf{r} n^{(0)}(\mathbf{r}) V(\mathbf{r})\right] + \frac{1}{2} \sum_{\mathbf{l},\mathbf{m},\alpha,\beta} u_{\mathbf{l}\alpha} u_{\mathbf{m}\beta} D_{\alpha\beta}(\mathbf{l} - \mathbf{m}) \tag{1.6}$$

is the vibration energy. Here, $\alpha, \beta = x, y, z$ and

$$D_{\alpha\beta}(\mathbf{l}-\mathbf{m}) = \frac{\partial^2}{\partial l_\alpha \partial m_\beta} \left[\frac{Z^2 e^2}{2} \sum_{\mathbf{l}' \neq \mathbf{m}'} \frac{1}{|\mathbf{l}'-\mathbf{m}'|} + \int \mathrm{d}\mathbf{r} n^{(0)}(\mathbf{r}) V(\mathbf{r}) \right] \tag{1.7}$$

is the dynamic matrix. EPI is given by

$$\begin{aligned} H_{\text{e–ph}} = & \sum_{\mathbf{l}} \mathbf{u}_{\mathbf{l}} \cdot \frac{\partial}{\partial \mathbf{l}} \int \mathrm{d}\mathbf{r} \left[\sum_s \Psi_s^\dagger(\mathbf{r}) \Psi_s(\mathbf{r}) - n^{(0)}(\mathbf{r}) \right] V(\mathbf{r}) \\ & + \frac{1}{2} \sum_{\mathbf{l},\mathbf{m},\alpha,\beta} u_{\mathbf{l}\alpha} u_{\mathbf{m}\beta} \frac{\partial^2}{\partial l_\alpha \partial m_\beta} \int \mathrm{d}\mathbf{r} \left[\sum_s \Psi_s^\dagger(\mathbf{r}) \Psi_s(\mathbf{r}) - n^{(0)}(\mathbf{r}) \right] V(\mathbf{r}), \end{aligned} \tag{1.8}$$

and the electron–electron correlations are described by

$$\begin{aligned} H_{\text{e–e}} = & \frac{1}{2} \int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \left[\sum_{ss'} \Psi_s^\dagger(\mathbf{r}) \Psi_{s'}^\dagger(\mathbf{r}') \Psi'_{s'}(\mathbf{r}') \Psi_s(\mathbf{r}) \right] \\ & - \int \mathrm{d}\mathbf{r} \left[\int \mathrm{d}\mathbf{r}' \frac{e^2 n^{(0)}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \mu_{\text{ex}}[n^{(0)}(\mathbf{r})] \right] \sum_s \Psi_s^\dagger(\mathbf{r}) \Psi_s(\mathbf{r}) \\ & + \frac{Z^2 e^2}{2} \sum_{\mathbf{l} \neq \mathbf{m}} \frac{1}{|\mathbf{l}-\mathbf{m}|}. \end{aligned} \tag{1.9}$$

We include the electrostatic repulsive energy of the nuclei in $H_{\text{e–e}}$, so that the average of $H_{\text{e–e}}$ is zero in the Hartree approximation.

1.3 Electron–Phonon Interaction in the Bloch Representation

The vibration Hamiltonian H_{ph} is a quadratic form and therefore can be diagonalized using the linear canonical transformation for the displacement operators:

$$\begin{aligned} \mathbf{u}_{\mathbf{l}} &= \sum_{\mathbf{q},\nu} \frac{\mathbf{e}_{\mathbf{q}\boldsymbol{\nu}}}{\sqrt{2NM\omega_{\mathbf{q}\nu}}} d_{\mathbf{q}\nu} \exp(\mathrm{i}\mathbf{q} \cdot \mathbf{l}) + \text{H.c.}, \\ \frac{\partial}{\partial \mathbf{u}_{\mathbf{l}}} &= \sum_{\mathbf{q},\nu} \mathbf{e}_{\mathbf{q}\boldsymbol{\nu}} \sqrt{\frac{M\omega_{\mathbf{q}\nu}}{2N}} d_{\mathbf{q}\nu} \exp(\mathrm{i}\mathbf{q} \cdot \mathbf{l}) - \text{H.c.}, \end{aligned} \tag{1.10}$$

where $\mathbf{q}$ is the phonon momentum, $d_{\mathbf{q}\nu}$ is the phonon (Bose) annihilation operator, $\mathbf{e}_{\mathbf{q}\boldsymbol{\nu}}$ and $\omega_{\mathbf{q}\nu}$ are the unit polarization vector and the phonon frequency, respectively, of the phonon mode ν, and H.c. is the Hermitian conjugate. Then, H_{ph} takes the following form

$$H_{\mathrm{ph}} = \sum_{\mathbf{q},\nu} \omega_{\mathbf{q}\nu}(d^{\dagger}_{\mathbf{q}\nu} d_{\mathbf{q}\nu} + 1/2), \tag{1.11}$$

if the eigenfrequencies $\omega_{\mathbf{q}\boldsymbol{\nu}}$ and the eigenstates $\mathbf{e}_{\mathbf{q}\boldsymbol{\nu}}$ satisfy

$$M\omega^2_{\mathbf{q}\boldsymbol{\nu}} e^{\alpha}_{\mathbf{q}\boldsymbol{\nu}} = \sum_{\beta} D^{\alpha\beta}_{\mathbf{q}} e^{\beta}_{\mathbf{q}\boldsymbol{\nu}}, \tag{1.12}$$

and

$$\sum_{\mathbf{q}} e^{*\alpha}_{\mathbf{q}\boldsymbol{\nu}} e^{\beta}_{\mathbf{q}\boldsymbol{\nu}} = N\delta_{\alpha\beta}. \tag{1.13}$$

The last equation and the bosonic commutation rules $[d_{\mathbf{q}\nu} d^{\dagger}_{\mathbf{q}'\boldsymbol{\nu}'}] = \delta_{\nu\nu'}\delta_{\mathbf{q}\mathbf{q}'}$ follow from $(\partial/\partial u^{\alpha}_{\mathbf{l}})u^{\beta}_{\mathbf{l}} - u^{\beta}_{\mathbf{l}}(\partial/\partial u^{\alpha}_{\mathbf{l}}) = \delta_{\alpha\beta}$. Here

$$D^{\alpha\beta}_{\mathbf{q}} = \sum_{\mathbf{m}} \exp(\mathrm{i}\mathbf{q}\cdot\mathbf{m}) D_{\alpha\beta}(\mathbf{m}) \tag{1.14}$$

is the Fourier transform of the second derivative of the ion potential energy. The first derivative in (1.6) is zero in crystals with a center of symmetry. Different solutions of (1.12) are classified with the phonon branch (mode) quantum number ν, which is $1, 2, 3$ for a simple lattice and $1, \ldots, 3k$ for a complex lattice with k ions per unit cell.

The periodic part of the Hamiltonian H_{e} is diagonal in the Bloch representation:

$$\Psi_s(\mathbf{r}) = \sum_{n,\mathbf{k}} \psi_{n\mathbf{k}s}(\mathbf{r}) c_{n\mathbf{k}s}, \tag{1.15}$$

where $c_{n\mathbf{k}s}$ are the fermion annihilation operators. The Bloch function obeys the Schrödinger equation

$$\left(-\frac{\nabla^2}{2m_{\mathrm{e}}} + V(\mathbf{r})\right)\psi_{n\mathbf{k}s}(\mathbf{r}) = E_{n\mathbf{k}s}\psi_{n\mathbf{k}s}(\mathbf{r}). \tag{1.16}$$

One-particle states are sorted with the momentum $\mathbf{k}$ in the Brillouin zone, band index n, and spin s. The solution of this equation allows us to calculate the periodic electron density $n^{(0)}(\mathbf{r})$, which determines the crystal field potential $V(\mathbf{r})$. LDA can explain the shape of the Fermi surface of wide-band metals and gaps in narrow-gap semiconductors. A spin-polarized version of LDA can explain a variety of properties of many magnetic materials. However, this is not the case for narrow d- and f-band metals and oxides (and other ionic lattices), where the electron–phonon interaction and Coulomb correlations are strong. These materials display much less band dispersion and wider gaps compared with the first-principle band structure calculations.

Using the phonon and electron annihilation and creation operators, the Hamiltonian is finally written as

$$H = H_{\mathrm{e}} + H_{\mathrm{e\text{–}ph}} + H_{\mathrm{e\text{–}e}}, \tag{1.17}$$

where

$$H_{\mathrm{e}} = \sum_{\mathbf{k},n,s} \xi_{n\mathbf{k}s} c^{\dagger}_{n\mathbf{k}s} c_{n\mathbf{k}s} + \sum_{\mathbf{q},\nu} \omega_{\mathbf{q}\nu} (d^{\dagger}_{\mathbf{q}\nu} d_{\mathbf{q}\nu} + 1/2) \tag{1.18}$$

describes independent Bloch electrons and phonons, $\xi_{n\mathbf{k}s} = E_{n\mathbf{k}s} - \mu$ is the band energy spectrum with respect to the chemical potential μ. The part of EPI, which is linear in the phonon operators, can be written as

$$H_{\mathrm{e\text{–}ph}} = \frac{1}{\sqrt{2N}} \sum_{\mathbf{k},\mathbf{q},n,n',\nu,s} \gamma_{nn'}(\mathbf{q},\mathbf{k},\nu) \omega_{\mathbf{q}\nu} c^{\dagger}_{n\mathbf{k}s} c_{n\mathbf{k}-\mathbf{q}s} d_{\mathbf{q}\nu} + \mathrm{H.c.}, \tag{1.19}$$

where

$$\gamma_{nn'}(\mathbf{q},\mathbf{k},\nu) = -\frac{N}{M^{1/2}\omega^{3/2}_{\mathbf{q}\nu}} \int \mathrm{d}\mathbf{r}\, (\mathbf{e}_{\mathbf{q}\nu} \cdot \nabla v(\mathbf{r}))\, \psi^{*}_{n\mathbf{k}s}(\mathbf{r}) \psi_{n'\mathbf{k}-\mathbf{q}s}(\mathbf{r}) \tag{1.20}$$

is the dimensionless matrix element. If we restrict the summations over $\mathbf{q}$ and $\mathbf{k}$ to the first Brillouin zone of the crystal, then $H_{\mathrm{e\text{–}ph}}$ should also include the summation over reciprocal lattice vectors $\mathbf{G}$ of umklapp scattering contributions where $\mathbf{q}$ is replaced by $\mathbf{q} + \mathbf{G}$. The terms of $H_{\mathrm{e\text{–}ph}}$ which are quadratic and of higher orders in the phonon operators are small. They play a role only for those phonons which are not coupled with electrons by the linear interaction (1.19).

The electron–electron correlation energy of a homogeneous electron system is often written as

$$H_{\mathrm{e\text{–}e}} = \frac{1}{2} \sum_{\mathbf{q}} V_{\mathrm{c}}(\mathbf{q}) \rho^{\dagger}_{\mathbf{q}} \rho_{\mathbf{q}}, \tag{1.21}$$

where $V_{\mathrm{c}}(\mathbf{q})$ is a matrix element, which is zero for $\mathbf{q} = 0$ because of electroneutrality and

$$\rho^{\dagger}_{\mathbf{q}} = \sum_{\mathbf{k},s} c^{\dagger}_{\mathbf{k}s} c_{\mathbf{k}+\mathbf{q}s} \tag{1.22}$$

is the density fluctuation operator. H should also include a random potential in doped semiconductors and amorphous metals, which might affect the EPI matrix element [6].

1.4 Electron–Phonon Interaction in the Wannier (Site) Representation

For the purpose of this review, we mostly confine our discussions to a single-band approximation with the EPI matrix element $\gamma_{nn}(\mathbf{q},\mathbf{k},\nu) = \gamma(\mathbf{q})$ depending only on the momentum transfer $\mathbf{q}$. The approximation allows for qualitative and in many cases quantitative descriptions of essential polaronic effects in advanced materials. Nevertheless, there might be degenerate atomic orbitals in solids coupled to local molecular-type Jahn–Teller distortions, where one has to consider multiband electron energy structures (see Sect. 3.6).

Quantitative calculations of the matrix element in the whole region of momenta have to be performed from pseudopotentials [1, 5]. On the other hand, one can parameterize EPI rather than to compute it from first principles in many physically important cases [7]. There are three most important interactions in doped semiconductors, which are polar coupling to optical phonons (i.e., the Fröhlich EPI), deformation potential coupling to acoustical phonons, and the local (Holstein) EPI with molecular-type vibrations in complex lattices. While the matrix element is ill defined in metals, the bare phonons $\omega_{\mathbf{q}\nu}$ and the electron band structure $E_{n\mathbf{k}}$ are well defined in doped semiconductors, which have their parent dielectric compounds. Here, the effect of carriers on the crystal field and on the dynamic matrix is small while the carrier density is much less than the atomic one. Hence, one can use the band structure and the crystal field of parent insulators to calculate the matrix element in doped semiconductors. The interaction constant $\gamma(\mathbf{q})$ has different q-dependence for different phonon branches. In the long-wavelength limit $(q \ll \pi/a)$, $\gamma(\mathbf{q}) \propto q^n$, where $n = -1, 0$ and $n = -1/2$ for polar optical, molecular ($\omega_{\mathbf{q}} = \omega_0$) and acoustic ($\omega_{\mathbf{q}} \propto q$) phonons, respectively. Not only q dependence is known, but also the absolute values of $\gamma(\mathbf{q})$ are well parameterized in this limit. For example in polar semiconductors, the interaction of two slow electrons at some distance r is found as (3.40)

$$v(r) = V_{\mathrm{c}}(r) - \frac{1}{N}\sum_{\mathbf{q}} |\gamma(\mathbf{q})|^2 \omega_{\mathbf{q}} \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}}. \tag{1.23}$$

The Coulomb repulsion in a rigid lattice is $V_{\mathrm{c}}(r) = e^2/\epsilon r$ and $|\gamma(\mathbf{q})|^2 = \gamma^2/q^2$, so that

$$v(r) = \frac{e^2}{\epsilon r} - \frac{\gamma^2 \omega_0}{4\pi r}. \tag{1.24}$$

On the other hand, the Coulomb repulsion can be expressed as $v(r) = e^2/\epsilon_0 r$, where the static dielectric constant, ϵ_0, describes screening by both core electrons and ions. The high frequency, ϵ, and static, ϵ_0, dielectric constants are measurable: ϵ is the square of the refractive index and ϵ_0 is the low-frequency dielectric function measured by putting the solid in a capacitor. Hence, the matrix element of the Fröhlich interaction depends only on the dielectric constants and the optical phonon frequency ω_0 as

$$|\gamma(\mathbf{q})|^2 = \frac{4\pi e^2}{\kappa \omega_0 q^2}, \tag{1.25}$$

where $\kappa = (\epsilon^{-1} - \epsilon_0^{-1})^{-1}$. If the crystal lacks an inversion center to be piezoelectric, there is EPI with piezoelectric acoustic phonons with an anysotropic matrix element, which also contribute to a coulombic-like attraction of two polarons [8].

To get a better insight into physical constraints of the above approximation, let us transform the Bloch states to the real space or Wannier states using the canonical linear transformation of the electron operators (here we follow [9]):

$$c_i = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \mathrm{e}^{\mathbf{ik \cdot m}} c_{\mathbf{k}s}, \tag{1.26}$$

where $i = (\mathbf{m}, s)$ includes both site $\mathbf{m}$ and spin s quantum numbers. In this site (Wannier) representation, the electron kinetic energy takes the following form

$$H_{\mathrm{e}} = \sum_{i,j} t(\mathbf{m} - \mathbf{n}) \delta_{ss'} c_i^{\dagger} c_j, \tag{1.27}$$

where

$$t(\mathbf{m}) = \frac{1}{N} \sum_{\mathbf{k}} E_{\mathbf{k}} \mathrm{e}^{\mathbf{ik \cdot m}}$$

is the "bare" hopping integral. Here, $j = (\mathbf{n}, s')$ and $E_{\mathbf{k}}$ is the Bloch band dispersion in the rigid lattice.

The electron–phonon interaction and the Coulomb correlations acquire simple forms in the Wannier representation, if their matrix elements in the momentum representation depend only on the momentum transfer $\mathbf{q}$:

$$H_{\text{e–ph}} = \sum_{\mathbf{q},i} \omega_{\mathbf{q}} \hat{n}_i \left[u_i(\mathbf{q}) d_{\mathbf{q}} + \mathrm{H.c.} \right], \tag{1.28}$$

$$H_{\text{e–e}} = \frac{1}{2} \sum_{i \neq j} V_{\mathrm{c}}(\mathbf{m} - \mathbf{n}) \hat{n}_i \hat{n}_j. \tag{1.29}$$

Here

$$u_i(\mathbf{q}) = \frac{1}{\sqrt{2N}} \gamma(\mathbf{q}) \mathrm{e}^{\mathbf{iq \cdot m}} \tag{1.30}$$

and

$$V_{\mathrm{c}}(\mathbf{m}) = \frac{1}{N} \sum_{\mathbf{q}} V_{\mathrm{c}}(\mathbf{q}) \mathrm{e}^{\mathbf{iq \cdot m}} \tag{1.31}$$

are the matrix elements of the electron–phonon and Coulomb interactions, respectively, in the Wannier representation for electrons, and $\hat{n}_i = c_i^{\dagger} c_i$ is the density operator.

We see that taking the interaction matrix element depending only on the momentum transfer, one neglects the terms in the electron–phonon and

Coulomb interactions, which are proportional to the overlap integrals of the Wannier orbitals on different sites. This approximation is justified for narrow-band materials, where the electron bandwidth is less than the characteristic magnitude of the crystal field potential. In the Wannier representation, the Hamiltonian becomes

$$\begin{aligned} H = &\sum_{i,j} t(\mathbf{m}-\mathbf{n})\delta_{ss'}c_i^\dagger c_j + \sum_{\mathbf{q},i}\omega_{\mathbf{q}}\hat{n}_i\left[u_i(\mathbf{q})d_{\mathbf{q}} + \text{H.c.}\right] \\ &+ \frac{1}{2}\sum_{i\neq j} V_{\text{c}}(\mathbf{m}-\mathbf{n})\hat{n}_i\hat{n}_j + \sum_{\mathbf{q}}\omega_{\mathbf{q}}(d_{\mathbf{q}}^\dagger d_{\mathbf{q}} + 1/2). \end{aligned} \tag{1.32}$$

One can transform it further using the site representation also for phonons. Replacing the Bloch functions in the definition of $\gamma(\mathbf{q})$ by their Wannier series yields

$$\gamma(\mathbf{q}) = -\frac{1}{M^{1/2}\omega_{\mathbf{q}}^{3/2}}\sum_{\mathbf{n}} \mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{n}}\mathbf{e}_{\mathbf{q}}\cdot\nabla_{\mathbf{n}}v(\mathbf{n}). \tag{1.33}$$

This result is obtained by neglecting the overlap integrals of the Wannier orbitals on different sites and by assuming that the single-ion potential $v(\mathbf{r})$ varies over the distance, which is much larger than the radius of orbits. Then using the displacement operators, one arrives at

$$H_{\text{e–ph}} = \sum_{\mathbf{m},\mathbf{n},s}\hat{n}_{\mathbf{m}s}\mathbf{u}_{\mathbf{n}}\cdot\nabla_{\mathbf{n}}v(\mathbf{m}-\mathbf{n}). \tag{1.34}$$

The site representation of $H_{\text{e–ph}}$ is particularly convenient for the interaction with dispersionless modes, when $\omega_{\mathbf{q}} = \omega_0$ and $\mathbf{e}_{\mathbf{q}} = \mathbf{e}$ are q-independent. Introducing the phonon site operators

$$d_{\mathbf{n}} = \frac{1}{\sqrt{N}}\sum_{\mathbf{q}}\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{n}}d_{\mathbf{q}}, \tag{1.35}$$

one obtains in this case

$$\mathbf{u}_{\mathbf{n}} = \frac{\mathbf{e}}{\sqrt{2M\omega_0}}(d_{\mathbf{n}} + d_{\mathbf{n}}^\dagger),$$

$$H_{\text{ph}} = \omega_0\sum_{\mathbf{n}}(d_{\mathbf{n}}^\dagger d_{\mathbf{n}} + 1/2),$$

and

$$H_{\text{e–ph}} = \omega_0\sum_{\mathbf{n},\mathbf{m},s} g(\mathbf{m}-\mathbf{n})(\mathbf{e}\cdot\mathbf{e}_{\mathbf{m}-\mathbf{n}})\hat{n}_{\mathbf{m}s}(d_{\mathbf{n}}^\dagger + d_{\mathbf{n}}), \tag{1.36}$$

where

$$g(\mathbf{m}) = \frac{1}{\omega_0\sqrt{2M\omega_0}}\frac{\mathrm{d}v(\mathbf{m})}{\mathrm{d}m}$$

is a dimensionless *force* acting between the electron on site $\mathbf{m}$ and the displacement of ion $\mathbf{n}$, and $\mathbf{e}_{\mathbf{m}-\mathbf{n}} \equiv (\mathbf{m}-\mathbf{n})/|\mathbf{m}-\mathbf{n}|$ is the unit vector in the direction from the electron **m** to the ion **n**. The real-space representation is particularly convenient in parameterizing EPI in complex lattices. Atomic orbitals of an ion adiabatically follow its motion. Therefore, the electron does not interact with the displacement of the ion, which orbitals it occupies, i.e., $g(0) = 0$.