1 Coulomb and Fröhlich interactions

1.1 Bare Hamiltonian

Superconductivity is a many-particle quantum phenomenon involving Coulomb electron–electron and electron–ion interactions. When these interactions are strong any ad hoc assumption of their range and relative magnitude might fail, since the dielectric response function of strongly correlated electrons is a priori unknown. Hence one has to start with a generic first-principles Hamiltonian including all unscreened Coulomb forces,

\[ H = -\sum_i \frac{\hbar^2 \nabla_i^2}{2m_e} + \frac{\alpha}{2} \sum_{i \neq i'} \frac{1}{|\mathbf{r}_i - \mathbf{r}_{i'}|} - Z\alpha \sum_{ij} \frac{1}{|\mathbf{r}_i - \mathbf{R}_j|} \]  \hspace{1cm} (1.1)

\[ + \frac{Z^2\alpha}{2} \sum_{j \neq j'} \frac{1}{|\mathbf{R}_j - \mathbf{R}_{j'}|} - \sum_j \frac{\hbar^2 \nabla_j^2}{2M} \]  \hspace{1cm} (1.2)

Here \( \mathbf{r}_i, \mathbf{R}_j \) are the electron and ion coordinates, respectively, \( i = 1, \ldots, N_e; \ j = 1, \ldots, N_i \); \( \nabla_i = \partial/\partial \mathbf{r}_i, \nabla_j = \partial/\partial \mathbf{R}_j \); \( Z e \) is the ion charge, \( \alpha = e^2/4\pi\epsilon_{\infty} (\epsilon_{\infty} \approx 8.85 \times 10^{-12} \text{ F/m is the vacuum permittivity}) \), and \( M \) is the ion mass. The system is neutral, so that \( N_e = ZN_i \).

The corresponding many-particle Schrödinger equation does not allow for a perturbative approach starting from a free-electron gas since the Coulomb interaction is strong. The ratio of the characteristic Coulomb energy to the electron kinetic energy is estimated as the dimensionless Wigner–Seitz radius \( r_s = 1.92\alpha/\hbar v_F \) (\( v_F \) is the Fermi velocity). Even in simple alkali metals it is \( r_s \approx 2.3 \) for \( v_F = 10^6 \text{ m/s} \), and it could be larger in complex narrow-band compounds. Hence any progress in the microscopic understanding of high-temperature superconductivity requires some simplifying physical ideas.

In this book we rely on overwhelming experimental evidence that most high-temperature superconductors are doped insulators or ‘poor metals’ where high-temperature superconductivity appears as a result of a chemical doping \( x \)
of parent ill-conducting compounds. Typical examples are cuprates, such as \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) (LSCO), \( \text{YBa}_2\text{Cu}_3\text{O}_{6+x} \) (YBCO), mercury–barium–calcium–copper oxides \( \text{HgBa}_2\text{Cu}_2\text{O}_{4+x} \) with maximum \( T_c = 135 \text{ K} \) at ambient pressure, alkali-doped fullerenes, \( \text{A}_x\text{C}_{60} \) (\( \text{A} = \text{K}, \text{Rb} \)), and, discovered more recently, ferropnictides, such as \( \text{FeAs-based superconductors SmFeAsO}_{1-x}\text{F}_x \) with \( T_c \) up to 55 K.

The electronic band structures and vibration (phonon) spectra of the parent compounds are reliably calculated using density functional theory (DFT), if one includes strong Coulomb correlations between electrons. While the \textit{ab initio} local-density approximation (LDA) is insufficient, adding the on-site Coulomb repulsion \( U \) to the LDA analysis within the LDA+U algorithm [23] or using LDA plus the tight-binding (cluster) approximation with the Coulomb correlations (the so-called LDA+GTB algorithm [24]), one can reproduce the correct antiferromagnetic ground state and the charge-transfer gap of the so-called charge-transfer Mott–Hubbard parent insulators such as \( \text{La}_2\text{CuO}_4 \) (LCO). These and other schemes [25] for the electronic structure found a charge-transfer gap at any doping of cuprates, pointing to a persistent Mott physics also at finite doping. This is in agreement with angle-resolved photoemission spectroscopy (ARPES) showing a clear departure from Fermi liquid behaviour in a wide doping range including the optimum doping where \( T_c \) is at a maximum [26]. Also the conventional adiabatic DFT underestimates the role of non-adiabatic effects, and therefore does not explain the optical infrared spectra and the electron–phonon coupling in doped cuprates. On the other hand, these spectra are well described within the non-adiabatic response approach [27] revealing a strong non-local polar electron–phonon interaction (EPI) in cuprates, together with the optical conductivity, as in an ionic insulator, even in the well-doped state. Some first-principles calculations have also found a strong EPI in ferropnictides [28].

Electrons are strongly coupled to nuclei and almost follow the ion motion in parent insulators. Still every individual ion can be polarised due to high-energy electron degrees of freedom of bound electrons. This electronic polarisation diminishes the Coulomb repulsion between doped carriers by a high-frequency dielectric constant \( \epsilon_\infty \). It can be calculated using the outlined first-principles methods or measured as the square of the refractive index of the insulator. Doped carriers repel each other via the reduced Coulomb potential \( \alpha/\epsilon_\infty|\mathbf{r}_i - \mathbf{r}_j| \) and interact with the individual ions of the parent insulator and with dopants via some pairwise potentials \( v_j(\mathbf{r}_i - \mathbf{R}_j) \) and \( v_d(\mathbf{r}_i - \mathbf{R}_d) \), respectively. Hence our ‘bare’ Hamiltonian is

\[
H = -\sum_i \frac{\hbar^2 \nabla_i^2}{2m_e} + \frac{\alpha}{2\epsilon_\infty} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i,j} v_j(\mathbf{r}_i - \mathbf{R}_j) + \sum_{i,d} v_d(\mathbf{r}_i - \mathbf{R}_d) + H_{\text{ins}},
\]

(1.3)
1.2 Harmonic approximation

where all sums count only the doped carriers, and $H_{\text{ins}}$ is the Hamiltonian of the parent insulator. This bare Hamiltonian accounts for all correlations between doped carriers and between the carriers and lattice vibrations. Along with vibration modes some parent insulators such as the Mott–Hubbard insulators have magnetic degrees of freedom (spin fluctuations) which are coupled with carriers when the insulator is doped. The role of these excitations for high-temperature superconductivity, extensively studied with some controversy [22], is discussed in Chapter 6 and Section 10.3.

1.2 Harmonic approximation

The Coulomb repulsion remains strong since a typical $\epsilon_\infty$ is only about two–five and ions are not frozen at any temperature so that one needs further approximations. One can take advantage of the large value of the mass ratio $M/m_e \gtrsim 10^4$. Ions are heavy and the amplitudes $|\langle u \rangle| \approx \sqrt{\hbar/M \omega}$ of their zero-point vibrations near equilibrium positions, $R_j \equiv l$, are much smaller than the lattice constant $a$,

$$\frac{|\langle u \rangle|}{a} \approx \left( \frac{m_e}{Mr} \right)^{1/4} \lesssim 1.$$  (1.4)

In this estimate we take the characteristic vibration frequency $\omega_0$ of the order of the ion plasmon frequency $\omega_0 \propto 1/\sqrt{M}$. According to this simplistic estimate relatively light elements such as oxygen in cuprate superconductors and carbon in graphite and doped fullerenes provide remarkably high-optical phonon frequencies on the order of $\hbar \omega_0 \gtrsim 80$ meV as observed in neutron scattering and other probes of phonon spectra. Because the vibration amplitudes are small we can expand the bare Hamiltonian, Eq. (1.3), in powers of $u$ up to quadratic terms inclusive, which is known as the harmonic approximation.

As long as the parent-insulator Hamiltonian, $H_{\text{ins}}$, is a quadratic form with respect to the displacements, it can be diagonalised with a linear canonical transformation,

$$u_i = \sum_{q,v} e_{qv} \left( \frac{\hbar}{2NM\omega_{qv}} \right)^{1/2} d_{qv} \exp(i\mathbf{q} \cdot \mathbf{l}) + \text{H.c.}, \quad (1.5)$$

$$\frac{\partial}{\partial u_i} = \sum_{q,v} e_{qv} \left( \frac{M\omega_{qv}}{2\hbar} \right)^{1/2} d_{qv} \exp(i\mathbf{q} \cdot \mathbf{l}) - \text{H.c.}.$$  

Here $d_{qv}$ is the phonon (Bose) annihilation operator, $e_{qv}$ and $\omega_{qv}$ are the unit polarization vector and the phonon frequency, respectively, $N$ is the number of unit cells, and H.c. is the Hermitian conjugate. Then $H_{\text{ins}}$ takes the harmonic oscillator form,

$$H_{\text{ins}} \approx H_{\text{ph}} = \sum_{q,v} \hbar \omega_{qv} (d_{qv}^\dagger d_{qv} + 1/2). \quad (1.6)$$
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The bosonic commutation rules \([d_{q_i} d_{q_i}^\dagger] = \delta_{q_i q_j} \delta_{qq}^\prime\) follow from \((\partial/\partial u_i^l) u_i^k - u_i^l (\partial/\partial u_i^l) = \delta_{ik}\) \((i, k = x, y, z)\). Different phonons are classified with the phonon quasi-momentum \(q\) in the first Brillouin zone (e.g. \(-\pi/a < q_i \leq \pi/a\) in a cubic lattice) and the phonon mode number \(\nu\), which is 1, 2, 3 in a simple lattice and 1, \ldots, \(3p\) in a lattice with \(p\) ions per unit cell.

The electron part of the Hamiltonian, Eq. (1.3), is conveniently expressed in terms of the electron field operators,

\[
H_e = \sum_s \int d^3r \Psi_s^\dagger (\mathbf{r}) \left[ -\frac{\hbar^2 \nabla^2}{2m_e} + V(\mathbf{r}) + \tilde{V}(\mathbf{r}) + \frac{\alpha}{2\varepsilon_\infty} \sum_{s'} d^3r' \frac{\Psi_{s'}(\mathbf{r}) \Psi_{s'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right] \Psi_s(\mathbf{r}),
\]

(1.7)
as well as the linear electron–phonon interaction,

\[
H_{e-ph} = -\sum_l \int d^3r \hat{n}(\mathbf{r}) \mathbf{u}_l \cdot \nabla v(\mathbf{r} - \mathbf{I}).
\]

(1.8)

Here \(V(\mathbf{r}) = \sum_\nu v(\mathbf{r} - \mathbf{I})\) is a periodic crystal field potential, \(\tilde{V}(\mathbf{r}) = \sum_d v_d(\mathbf{r} - \mathbf{R}_d)\) is a change in the crystal field caused by doping which is often random, and \(\hat{n}(\mathbf{r}) = \sum_s \Psi_s^\dagger (\mathbf{r}) \Psi_s(\mathbf{r})\) is the carrier density operator. The terms of \(H_{e-ph}\) quadratic and higher orders in displacements are small. They have a role to play only for those phonons which are not coupled with electrons by the linear interaction, Eq. (1.8).

The field operators can be expanded in any complete set of single-particle eigenstates, for instance in the Bloch-function set,

\[
\Psi_s(\mathbf{r}) = \sum_{k,n,s} \psi_n^k s(\mathbf{r}) c_{nk}s,
\]

(1.9)

where \(c_{nk}s\) annihilates a fermion with quasi-momentum \(k\) and spin \(s\) in the energy band labelled by \(n\). The Bloch functions diagonalise the periodic part of the single-particle Schrödinger equation

\[
\left( -\frac{\hbar^2 \nabla^2}{2m_e} + V(\mathbf{r}) \right) \psi_n^k s(\mathbf{r}) = E_n^k s \psi_n^k s(\mathbf{r}),
\]

(1.10)

providing the electron band structure of the doped insulator, \(E_n^k s\).

1.3 Generic Hamiltonian in the Wannier representation

For narrow-band compounds with a strong Coulomb repulsion and a strong EPI it is more convenient to use the Wannier (site) wavefunctions instead of the Bloch
1.3 Generic Hamiltonian in the Wannier representation

states defined as

\[ w_{nm,s}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_k e^{-i\mathbf{k} \cdot \mathbf{m}} \psi_{nks}(\mathbf{r}), \tag{1.11} \]

where \( \mathbf{m} \) stands for the crystal-lattice site position vector. The Wannier wavefunctions are orthogonal and normalised,

\[ \int d\mathbf{r} w^*_{nm,s}(\mathbf{r}) w_{n'm's'}(\mathbf{r}) = \delta_{m,m'} \delta_{n,n'} \delta_{s,s'} \tag{1.12} \]

because the Bloch functions are orthogonal and normalised.

An advantage of the Wannier functions is in their small extension compared with the lattice constant in complex narrow-band compounds so that one can use a tight-binding approximation (TBA). The idea behind TBA is to fit the band dispersion calculated using the first-principles DFT with a finite number of hopping integrals. Many electronic structures, in particular perovskites, can be fitted with only the nearest-neighbour matrix elements between \( s \)-, \( p \)-, and \( d \)-like orbitals. The hopping integrals could not be calculated by using tabulated atomic wavefunctions and potentials estimated for various solids. True atomic orbitals are not orthogonal for different sites and they do not provide a quantitative description of bands in solids. On the other hand, atomic-like Wannier orbitals Eq. (1.11) can provide a very good description already in the nearest-neighbour TBA.

Substituting the field operators expressed in terms of the Wannier orbitals, \( \Psi_s(\mathbf{r}) = \sum_{m,n,s} w_{nm,s}(\mathbf{r}) c_{nm,s} \) in Eqs. (1.7), (1.8) and keeping only major terms in both interactions, diagonal with respect to sites, yield the generic Hamiltonian describing high-temperature superconductivity,

\[ H = -\sum_{i,j} (T_{ij} \delta_{ss'} + \mu \delta_{ij}) c_i^\dagger c_j + \frac{\alpha}{2\epsilon_\infty} \sum_{i \neq j} \hat{n}_i \hat{n}_j + \sum_{\mathbf{q},\nu,i} \hbar \omega_{\mathbf{q},\nu} \hat{n}_i \left[ u_i(\mathbf{q}, \nu) d_{\mathbf{q} \nu} + \text{H.c.} \right] + H_{\text{ph}}. \tag{1.13} \]

Here

\[ T_{ij} = \int d\mathbf{r} u^*_m(\mathbf{r}) \left[ -\frac{\hbar^2 \nabla^2}{2m_e} + V(\mathbf{r}) + \tilde{V}(\mathbf{r}) \right] u_n(\mathbf{r}) \tag{1.14} \]

is the bare hopping integral, if \( \mathbf{m} \neq \mathbf{n} \), or the site energy, if \( \mathbf{m} = \mathbf{n} \), \( \mu \) is the chemical potential, \( i = \mathbf{m}, s \) and \( j = \mathbf{n}, s' \) include both site \( (\mathbf{m}, \mathbf{n}) \) and spin \( (s, s') \) quantum numbers, \( c_i, d_{\mathbf{q} \nu} \) are electron and phonon operators, respectively, and \( \hat{n}_i = c_i^\dagger c_i \) is a site occupation operator.

The EPI matrix element is

\[ u_i(\mathbf{q}, \nu) = (2N)^{-1/2} \gamma(\mathbf{q}, \nu) \exp(i \mathbf{q} \cdot \mathbf{m}) \tag{1.15} \]
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with the dimensionless EPI coupling,

\[ \gamma(q, \nu) = (\hbar M \omega_{q,\nu}^3)^{-1/2} \sum_{l \neq 0} e^{iq \cdot l} e_{q,\nu} \cdot \nabla v(l). \] (1.16)

1.4 Fröhlich EPI in doped polar insulators

Deriving the generic Hamiltonian, Eq. (1.13), in the site representation we approximate the Wannier orbitals as delta functions, this is justified as long as the characteristic wavelength of phonons and doped carriers significantly exceeds the orbital size \( a_0 \ll a \). The singular on-site \( (m = n) \) Coulomb repulsion of two carriers with opposite spins (the Hubbard \( U \)) is infinite in this approximation. In fact, it should be cut at \( \approx \alpha/\epsilon_{\infty}a_0 \) as indicated by the bar above the sum, \( \bar{\sum} \). Also for mathematical transparency we consider a single electron band dropping the electron band index which is sufficient for understanding the high-temperature superconductivity of most compounds.

Quantitative calculations of the EPI matrix elements in semiconductors and metals have to be performed numerically from pseudopotentials [29, 30]. Fortunately one can parametrise the EPI rather than compute it in many physically important cases [31]. The EPI in ionic lattices such as the cuprates is dominated by coupling with polar optical phonons. This dipole interaction is much stronger than the deformation potential coupling to acoustic phonons and other multipole EPIs. While the EPI matrix elements are ill-defined in metals, they are well-defined in doped insulators, which have their parent dielectric compounds with well-defined phonon frequencies \( \omega_{q,\nu} \) and the electron band dispersion \( E_k \).

To parametrise the EPI coupling let us consider a doped lattice with no hopping between sites, \( T_{ij} = 0 \). The many-particle Hamiltonian of this system allows for exact diagonalisation by shifting the equilibrium ion positions (i.e. changing the phonon vacuum). Indeed replacing the phonon operators in Eq. (1.13) for new ones, \( \tilde{d}_{q,\nu} \),

\[ d_{q,\nu} = \tilde{d}_{q,\nu} + \sum_i \tilde{n}_i u_i^*(q, \nu), \] (1.17)

one obtains

\[ H = - \sum_i (E_p + \mu) \hat{n}_i + \sum_{i \neq j} v_{ij} \hat{n}_i \hat{n}_j + \tilde{H}_{ph}, \] (1.18)

where

\[ E_p = \frac{1}{2N} \sum_{q,\nu} |\gamma(q, \nu)|^2 \hbar \omega_{q,\nu} \] (1.19)
1.4 Fröhlich EPI in doped polar insulators

is a polaronic level shift (or the polaron binding energy),

\[ v_{ij} = \frac{\alpha}{\epsilon_\infty|m-n|} - \frac{1}{N} \sum_{q,v} |\gamma(q,v)|^2 \hbar \omega_{qv} \cos[q \cdot (m-n)] \]  

(1.20)

is the interaction between localised carriers including their direct Coulomb repulsion and the interaction via the local lattice deformation, and

\[ \tilde{H}_{ph} = \sum_{q,v} \hbar \omega_{qv} (\tilde{d}_q^\dagger \tilde{d}_{qv} + 1/2). \]  

(1.21)

All eigenstates and eigenvalues of the diagonal many-particle Hamiltonian Eq. (1.18) are readily found. The eigenstates \( |\tilde{N}\rangle = |n_i, n_{qv}\rangle \) are sorted by the polaron \( n_m \) and phonon \( n_{qv} \) occupation numbers, and the energy levels are

\[ E = -(\mu + E_p) \sum_i n_i + \frac{1}{2} \sum_{i \neq j} v_{ij} n_i n_j + \sum_q \hbar \omega_{qv} (n_{qv} + 1/2), \]  

(1.22)

where \( n_i = 0, 1 \) and \( n_{qv} = 0, 1, 2, 3, \ldots, \infty \). It describes localised polarons and independent phonons, which are vibrations of ions relative to new equilibrium positions. The phonon frequencies remain unchanged. The middle of the electron band falls down by the polaron level shift \( E_p \) due to a potential well created by the lattice deformation.

On the other hand, two static carriers in the ionic lattice repel each other with the Coulomb potential

\[ v_{ij} = \frac{\alpha}{\epsilon_0|m-n|}, \]  

(1.23)

where the static dielectric constant, \( \epsilon_0 \), accounts for the screening by both core electrons and ions. Comparing Eq. (1.20) and Eq. (1.23) we find

\[ \sum_{q,v} |\gamma(q,v)|^2 \hbar \omega_{qv} = \frac{4\pi \alpha}{\kappa V_0 a^2}, \]  

(1.24)

at relatively small \( q \leq 1/a \). Here \( V_0 \) is the unit cell volume and \( \kappa = \epsilon_0 \epsilon_\infty / (\epsilon_0 - \epsilon_\infty) \).

The static dielectric constant \( \epsilon_0 \) is readily measured by putting the parent insulator in a capacitor. Hence, different from many models of high-temperature superconductors proposed so far, all parameters of our generic Hamiltonian, Eq. (1.13), are defined through the material parameters. In particular, the dielectric constants as well as the optical phonon frequencies and the bare hopping integrals in a rigid lattice can be measured and/or calculated with DFT in the parent insulator.

The long-wavelength approximation, Eq. (1.24), allows for a fair estimate of the polaron level shift \([32, 33, 34], E_p\), and of the attraction of two carriers induced by
Table 1.1 Polaron level shift [34].

<table>
<thead>
<tr>
<th>System</th>
<th>$\epsilon_\infty$</th>
<th>$\epsilon_0$</th>
<th>$a \times b \times c$ (Å$^3$)</th>
<th>$E_p$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrTiO$_3$</td>
<td>5.2</td>
<td>310</td>
<td>3.905$^3$</td>
<td>0.852</td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>5.1–5.3</td>
<td>1499</td>
<td>3.992$^2 \times 4.032$</td>
<td>0.842</td>
</tr>
<tr>
<td>BaBiO$_3$</td>
<td>5.7</td>
<td>30.4</td>
<td>4.34$^2 \times 4.32$</td>
<td>0.579</td>
</tr>
<tr>
<td>La$_2$CuO$_4$</td>
<td>5.0</td>
<td>30</td>
<td>3.8$^2 \times 6$</td>
<td>0.647</td>
</tr>
<tr>
<td>LaMnO$_3$</td>
<td>3.9</td>
<td>16</td>
<td>3.86$^3$</td>
<td>0.884</td>
</tr>
<tr>
<td>La$_{2-x}$Sr$_x$+2$^+$Mn$_2$O$_7$</td>
<td>4.9</td>
<td>38</td>
<td>3.86$^2 \times 3.9$</td>
<td>0.807</td>
</tr>
<tr>
<td>NiO</td>
<td>5.4</td>
<td>12</td>
<td>4.18$^3$</td>
<td>0.429</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>6–7.2</td>
<td>89–173</td>
<td>4.59$^2 \times 2.96$</td>
<td>0.643</td>
</tr>
<tr>
<td>MgO</td>
<td>2.964</td>
<td>9.816</td>
<td>4.2147$^3$</td>
<td>0.982</td>
</tr>
<tr>
<td>CdO</td>
<td>5.4</td>
<td>21.9</td>
<td>4.7$^3$</td>
<td>0.522</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>5</td>
<td>100–300</td>
<td>7.31$ \times 7.54 \times 7.7$</td>
<td>0.445</td>
</tr>
<tr>
<td>NaCl</td>
<td>2.44</td>
<td>5.90</td>
<td>5.643$^3$</td>
<td>0.749</td>
</tr>
<tr>
<td>EuS</td>
<td>5.0</td>
<td>11.1</td>
<td>5.968$^3$</td>
<td>0.324</td>
</tr>
<tr>
<td>EuSe</td>
<td>5.0</td>
<td>9.4</td>
<td>6.1936$^3$</td>
<td>0.266</td>
</tr>
</tbody>
</table>

The Fröhlich EPI, which is about $2E_p$, is given by

$$E_p \approx \frac{2\pi \alpha}{\kappa} \int_{BZ} \frac{dq}{(2\pi)^3 q^2}. \quad (1.25)$$

Here the size of the integration region, which is the Brillouin zone (BZ), is determined by the lattice constants $-\pi/a < q_x \leq \pi/a$, $-\pi/b < q_y \leq \pi/b$, and $-\pi/c < q_z \leq \pi/c$. As one can see from Table 1.1 the Fröhlich EPI alone could provide the binding energy of two holes of more than 1 eV in cuprates. In fact, Eq. (1.25) underestimates the polaron binding energy, since the deformation potential and molecular-type (e.g. Jahn–Teller [35]) EPIs are not included in the estimate.

There are two important conclusions which one can infer from the outlined analysis: (a) the polar lattice deformation contributes to the binding energy of two carriers by one order of magnitude more than a possible magnetic interaction, whose contribution is estimated as 0.1 eV [22], and (b) the static Fröhlich EPI almost nullifies the Coulomb repulsion because of the large static dielectric constant $\epsilon_0 \gg 1$ of the parent insulators so that the residual repulsion of two static carriers, Eq. (1.23), is significantly reduced, or even almost nullified with respect to the bare Coulomb repulsion.
Small polarons

2.1 Canonical transformations

Our generic Hamiltonian, Eq. (1.13), with carrier kinetic energy and strong Coulomb and Fröhlich interactions does not allow for any ad hoc assumption about the range of both interactions and the relative magnitudes of the three energies, since dynamic response functions of strongly correlated carriers are a priori unknown. But in the strong-coupling regime, when the interactions dominate over the kinetic energy, we can integrate them out with a canonical transformation.

Various canonical transformations serve as a powerful tool in polaron theory [36]. Using an appropriate transformation one can approximately diagonalise the Hamiltonian of strongly coupled electrons and phonons and then apply perturbation theory with respect to the residual off-diagonal terms. The philosophy of the method is simple. We are looking for a complete orthonormal set of multi-particle eigenstates $|n\rangle$, which obey the steady state Schrödinger equation

$$H |n\rangle = E_n |n\rangle.$$  \hspace{1cm} (2.1)

There exists a unitary transformation $U$ such that the eigenstates $|n\rangle$ may be generated from another arbitrary complete orthonormal set $|\tilde{n}\rangle$,

$$|n\rangle = U |\tilde{n}\rangle.$$  \hspace{1cm} (2.2)

The requirement that the states generated by Eq. (2.2) form an eigenbase of the given Hamiltonian $H$ is equivalent to the condition that the transformed Hamiltonian $\tilde{H}$ is diagonal with respect to $|\tilde{n}\rangle$:

$$\tilde{H} |\tilde{n}\rangle = E_n |\tilde{n}\rangle.$$  \hspace{1cm} (2.4)

The orthogonality should be conserve, $\langle n | n' \rangle = \langle \tilde{n} | U^\dagger U | \tilde{n}' \rangle = \delta_{nn'}$ so that

$$U^\dagger = U^{-1}.$$  \hspace{1cm} (2.5)
Small polarons

2.2 Lang–Firsov canonical transformation

A transformation frequently employed in polaron theory is the displacement transformation introduced by Lee, Low and Pines [37] for a single continuum polaron and by Lang and Firsov (LF) [38] for a single lattice polaron. We shall adopt it here for the multi-polaron system. The LF transformation displaces ions to new equilibrium positions depending on the electron coordinates,

\[ U = e^{-S} \]  

(2.6)

where

\[ S = \sum_{q,v,i} \hat{n}_i \left[ u_i^*(q,v) d_{qv} - \text{H.c.} \right] \]  

(2.7)

is such that \( S^\dagger = S^{-1} = -S \). The electron and phonon operators are transformed as

\[ \tilde{c}_i = e^S c_i e^{-S}, \]  

(2.8)

\[ \tilde{d}_{qv} = e^S d_{qv} e^{-S}. \]  

(2.9)

We can simplify these equations by rescaling all matrix elements by the same amount, \( u_i(q,v) \rightarrow \eta u_i(q,v) \) and differentiating the transformed operators with respect to the scaling parameter \( \eta \) as

\[ \frac{\partial \tilde{c}_i}{\partial \eta} = \sum_{q,v} e^S [\hat{n}_i, c_i] (u_i^*(q,v) d_{qv} - u_i(q,v) d_{qv}) e^{-S}, \]  

(2.11)

\[ \frac{\partial \tilde{d}_{qv}}{\partial \eta} = \sum_i e^S \hat{n}_i u_i^*(q,v) [d_{qv}, d_{qv}] e^{-S}. \]  

(2.12)

Using commutators \([\hat{n}_i, c_i] = -c_i, [d_{qv}^\dagger, d_{qv}] = -1\), and \([\hat{n}_i, S] = 0\) we find

\[ \frac{\partial \tilde{c}_i}{\partial \eta} = -\tilde{c}_i \sum_{q,v} \left( u_i^*(q,v) d_{qv} - u_i(q,v) d_{qv} \right), \]  

(2.11)

\[ \frac{\partial \tilde{d}_{qv}}{\partial \eta} = -\sum_i \hat{n}_i u_i^*(q,v). \]

The solutions of these differential equations respecting the ‘boundary’ conditions \( d_{qv} = d_{qv} \) and \( \tilde{c}_i = c_i \) for \( \eta = 0 \) are

\[ \tilde{c}_i = c_i \exp \left[ \eta \sum_{q,v} (u_i(q,v) d_{qv} - u_i^*(q,v) d_{qv}^\dagger) \right], \]  

(2.12)