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**LETTER TO THE EDITOR**

# Large polarons with quadratic electron–phonon interaction

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**Abstract.** The Fröhlich Hamiltonian of large polarons with quadratic electron–phonon interaction is obtained and the ground-state energy is calculated by using second-order perturbation theory.

The polaron concept as usually understood arises from the consideration of the *linear* interaction of a *single* electron, moving *slowly* in the conduction band of an otherwise *insulating* material, with the longitudinal optical phonon field of the associated *ionic* lattice. The electron distorts and displaces its surrounding ions, establishing a polarisation field in the crystal, which acts back on the electron whose properties are then modified; in particular, the electron acquires a self-energy and an enhancement of its Bloch effective mass. In the language of field theory these effects arise from the emission and reabsorption of virtual quanta of the longitudinal optical phonon field of the material [1].

Of the above five conditions that characterise the conventional polaron only the first is satisfied exactly, and the others are not always taken into account in existing studies (see [2] and references therein). The purpose of this Letter is to consider electron–phonon interaction with linear and quadratic terms in the phonon coordinates, and to calculate the ground-state energy of a large polaron within second-order perturbation theory.

The polaron problem is usually formulated in terms of the Fröhlich Hamiltonian (FH), whose important characteristics are the linearity of the electron–phonon interaction and the approximation of treating the lattice as a continuum. A clear and *ab initio* derivation of this Hamiltonian has been given in [3]. However, it is difficult to include non-linear interaction in the FH in this procedure and we will therefore follow a different approach [4].

The total Hamiltonian $H = H_0 + H_1$, is made up of two terms. The first one, $H_0$, is the sum of one electron and free phonons, and will be described by

$$H_0 = \frac{p^2}{2m} + \sum_q \hbar\omega_q b_q^+ b_q \tag{1}$$

where $\boldsymbol{p} = \hbar\boldsymbol{k}$ is the electron momentum with bare mass $m$ and the $b_q^+$ ($b_q$) are the creation (annihilation) operators for a LO phonon with wavevector $\boldsymbol{q}$ and energy $\hbar\omega_q$.

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The second term $H_1$, corresponding to the interaction of the electron with ions and phonons, can be expressed in second-quantised notation as follows:

$$H_1 = \sum_{k,k',1} \langle \boldsymbol{k}|V(\boldsymbol{r} - \boldsymbol{R}_1 - \boldsymbol{y}_1)|\boldsymbol{k}'\rangle c_k^+ c_{k'} = \sum_{k,k',1} \exp[\mathrm{i}(\boldsymbol{k}' - \boldsymbol{k}) \cdot (\boldsymbol{R}_1 + \boldsymbol{y}_1)] V_{k-k'} c_k^+ c_{k'} \quad (2)$$

where $V(\boldsymbol{r} - \boldsymbol{R}_1)$ is the ionic potential at the site $\boldsymbol{R}_1$, and the $c_k^+$ ($c_k$) are the creation (annihilation) operators for the electron. If the displacement $\boldsymbol{y}_1$ of the ion at $\boldsymbol{R}_1$ is sufficiently small we can expand the exponential and keep terms up to the quadratic ones in (2):

$$\exp[\mathrm{i}(\boldsymbol{k} - \boldsymbol{k}) \cdot \boldsymbol{y}_1] = 1 + \mathrm{i}(\boldsymbol{k}' - \boldsymbol{k}) \cdot \boldsymbol{y}_1 - \tfrac{1}{2}[(\boldsymbol{k}' - \boldsymbol{k}) \cdot \boldsymbol{y}_1]^2$$

and taking

$$\boldsymbol{y}_1 = \frac{1}{\sqrt{N}} \sum_q \boldsymbol{y}_q \, \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}_1} = \frac{1}{\sqrt{N}} \sum_q \left(\frac{\hbar}{2M\omega_q}\right)^{1/2} (b_{-q}^+ + b_q) \, \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}_1}$$

equation (2) becomes

$$H = N \sum_{k,k',1} \exp[\mathrm{i}(\boldsymbol{k}' - \boldsymbol{k}) \cdot \boldsymbol{R}_1] \, V_{k-k'} c_k^+ c_{k'} + \frac{\mathrm{i}}{\sqrt{N}} \sum_{k,k'} (\boldsymbol{k}' - \boldsymbol{k}) \cdot \boldsymbol{y}_{k-k'} V_{k-k'} c_k^+ c_{k'}$$

$$- \frac{1}{2N} \sum_{k,k'} [(\boldsymbol{k}' - \boldsymbol{k}) \cdot \boldsymbol{y}_{k-k'}]^2 \, V_{k-k'} c_k^+ c_{k'} \quad (3)$$

where only the longitudinal phonon modes are considered. The first term in (3) is independent of the lattice displacements and can be added to $H_0$, so the bare electron mass $m$ is now replaced by the Bloch effective mass.

If we assume that $V_{k-k'}$ is given by

$$V_{k-k'} = -4\pi e e^*/V|\boldsymbol{k} - \boldsymbol{k}'|^2 \quad (4)$$

with an effective ionic charge $e^*$ [5]

$$(e^*)^2 = (VM\omega_q^2/4\pi N)(1/\varepsilon_\infty - 1/\varepsilon_0) \quad (5)$$

where $M$ is the reduced ionic mass and $\varepsilon_\infty$ and $\varepsilon_0$ are dielectric constants of the medium, we can immediately obtain the interaction term of the FH and a new term representing the non-linear electron–phonon interaction. Thus the modified FH becomes

$$H = \frac{p^2}{2m} + \sum_q \hbar\omega_0 b_q^+ b_q + \sum_q M_q (b_q^+ \, \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} + \mathrm{HC})$$

$$+ \sum_{q,q'} M_q' (b_q^+ \, \mathrm{e}^{-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} + \mathrm{HC})(b_{q'}^+ \, \mathrm{e}^{-\mathrm{i}\boldsymbol{q}'\cdot\boldsymbol{r}} + \mathrm{HC}) \quad (6)$$

where

$$M_q = \mathrm{i}(\hbar\omega_0/qu^{1/2})(4\pi\alpha/V)^{1/2} \quad (7a)$$

and

$$M_q' = \alpha\hbar^2\omega_0^2/2Nuee^*. \quad (7b)$$

Here $V$ is the volume of the system, $\alpha$ is called the coupling constant, showing the electron–phonon coupling strength, and $u = (2m\omega_0/\hbar)^{1/2}$. In (6) the LO phonons are assumed to be dispersionless, i.e. $\omega_q = \omega_0$.

It should be pointed out that with this choice of $V_{k-k'}$ in the form of (4), $M_q$ is proportional to $1/q$ as expected for LO phonons and $M'_q$ is independent of $\boldsymbol{q}$, which considerably simplifies our calculations.

Even without the non-linear term, the FH has not been exactly solved so far. Fröhlich and co-workers [6] have approximately solved the polaron problem for weak coupling strength, that is for $\alpha < 1$. $H_0$ is the unperturbed part of the Hamiltonian which gives the ground-state energy $E_0$ and $H_1$ will be treated as a perturbation, and the second-order correction to $E_0$ is given by

$$\Delta E_i = -\sum_i \frac{|\langle 0|H_1|i\rangle|^2}{E_i - E_0} \tag{8}$$

where the $|i\rangle$ are intermediate states. In our case, only the $b_q^+ b_{q'}^+|0\rangle$ term will contribute to the energy and a new term

$$\Delta E_2' = -\sum_{q,q'} |M'_q|^2 \left(\frac{|\boldsymbol{p} - \hbar(\boldsymbol{q} + \boldsymbol{q}')|^2}{2m} + 2\hbar\omega_0 - \frac{p^2}{2m}\right)^{-1} \tag{9}$$

will be added to the well known perturbation result.

For low electron momentum $\boldsymbol{p}$, the sum in (9) can be expanded as a power series in $\boldsymbol{p}$; on changing the sums over $\boldsymbol{q}$ and $\boldsymbol{q}'$ to integrals, one obtains for the ground-state energy

$$E = -\alpha(\hbar\omega_0)(A + CI) + (p^2/2m)[1 - (\alpha/6)B - \alpha CJ] \tag{10}$$

where $C = (2m/M)\, Vu^3/8\pi^3 N$,

$$I = \frac{1}{u^4}\int\int qq' \ln\left(\frac{(q+q')^2 + 2u^2}{(q-q'^2) + 2u^2}\right) \mathrm{d}q\, \mathrm{d}q'$$

and

$$J = \frac{1}{u^2\pi^2}\int\int \frac{(q\cos\theta + q'\cos\theta')^2\, \mathrm{d}^3q\, \mathrm{d}^3q'}{(q^2 + q'^2 + 2qq'\cos\Gamma + 2u^2)^3}$$

with $\cos\Gamma = \cos\theta\cos\theta' + \sin\theta\sin\theta'\cos(\varphi - \varphi')$.

The integrals $I$ and $J$ diverge if one takes upper limits for $q$ and $q'$ as infinite. We therefore have an upper cut-off $q_c$ given by the maximum allowed phonon wavevector. Although the medium is treated as continuum in the FH, due to the discreteness of the lattice such a natural cut-off $q_c$, where $1/q_c$ is of the order of the lattice spacing, will be realistic. In fact, the discreteness of the lattice was to a certain degree incorporated into the Hamiltonian in the same way for the problem of the polaron self-trapping transition [7–9]. The constants $A$ and $B$ are fairly close to unity for a finite $q_c$ and equal to unity in the $q_c \to \infty$ limit as expected.

Since a polaron is spread over many lattice cells in the continuum approximation, it is customary to define a polaron radius $r_p$, which turns out to be equal to $1/u$. The value of $r_p$ for alkali and silver halides is between 10 and 20 Å; for II–VI and III–V semiconductors it is about 100 Å. The latter materials have small $\alpha$-values; therefore they are very convenient for applying our results to.

In (10), $m/M$ is of the order of $10^{-4}$ and $V/N$ is the volume of the unit cell. If we take $r_p = 20a$ and $q_c = 2\pi/a$ in the integrals $I$ and $J$, the shift in the self-energy will be about 3%, while the change in the effective mass is negligible.

Although this result appears as a small correction to the ground-state energy, there may be cases where the non-linear electron–phonon interaction can give interesting results, as in recent papers for acoustical polaron mobility [10] and quasi-one-dimensional organic conductors [11].

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