THE QUANTUM STATES OF PARTICLES COUPLED WITH ARBITRARY STRENGTH TO A HARMONICALLY OSCILLATING CONTINUUM. II. THE CASE OF TRANSLATIONAL SYMMETRY

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The method developed in the preceding paper[1] is extended to the case of a system with translational symmetry (there is no external potential field and the particle is not localized). The variational method is used to calculate the lowest energy levels and wave functions of the system described by the Hamiltonian of Eqs. (1) and (2). The trial function is chosen in the form given by Eqs. (5) and (6). This method is applied to the polaron problem. In the limiting cases of weak and strong coupling between the particle and oscillations the calculated energy agrees with the exact result of perturbation theory (in the second approximation) and approaches Feynman's result for strong coupling.[2]

In a previous article[1] we have treated particles interacting with a harmonically oscillating continuum while in a particle-localizing external potential field. This latter field removed the translational symmetry. In the present article we shall treat the problem without this external field, so that the particle may move through all space. It is assumed that the Hamiltonian of the system is of the form

$$H = -\frac{\hbar^2}{2m}\Delta + \frac{1}{2}\sum_{\varkappa}\hbar\omega_{\varkappa}(q_{\varkappa}^2 - \partial^2/\partial q_{\varkappa}^2) + \sum_{\varkappa} c_{\varkappa} q_{\varkappa} \chi_{-\varkappa}(\mathbf{r}). \quad (1)$$

Here $\mathbf{r}$ is the radius vector of the particles, m is its mass, the ω_κ are the natural frequencies of the continuum, κ is the wave vector of the continuum oscillation, the q_κ are the normal coordinates of these oscillations, the c_κ are the coupling constants of the particle with these oscillations, and

$$\chi_{\varkappa}(\mathbf{r}) = \sqrt{2/V}\sin(\varkappa\mathbf{r} + \pi/4). \quad (2)$$

The $\chi_\kappa(\mathbf{r})$ form a complete system of orthonormal functions in the fundamental volume V of the periodicity, a volume chosen in the form of a cube. Such a Hamiltonian is obtained, for instance, when the motion of a conduction electron interacting with crystal lattice vibrations is considered. A similar Hamiltonian occurs for a particle interacting with a quantized field.

1. CHOICE OF THE TRIAL FUNCTION AND DETERMINATION OF THE FUNCTIONAL $\overline{\overline{H}}$

Ordinarily, the continuum oscillations with wave vectors κ and $-\kappa$ have the same frequency and coupling constant, so that we may write $c_\kappa = c_{-\kappa}$ and $\omega_\kappa = \omega_{-\kappa}$. The normal coordinates q_κ are usually the coefficients of the Fourier expansion of the deformation of the medium or field. In the present case we shall expand in terms of the basis functions given in Eq. (2). Let the translation operator $T_{\mathbf{a}}$ denote the following change in the configuration of the system: the particle and the whole deformation of the medium undergo a space translation by the vector $\mathbf{a}$. Explicitly, the definition of $T_{\mathbf{a}}$ is

$$T_{\mathbf{a}} f(\mathbf{r}, q_{\varkappa}, q_{-\varkappa}) = f(\mathbf{r} + \mathbf{a}, q_{\varkappa}\cos\varkappa\mathbf{a} - q_{-\varkappa}\sin\varkappa\mathbf{a}, q_{-\varkappa}\cos\varkappa\mathbf{a} + q_{\varkappa}\sin\varkappa\mathbf{a}). \quad (3)$$

It is easily shown that H is invariant under such a translation. Thus the exact wave functions of the system may be chosen, as is well known, so that they be eigenfunctions of all the $T_{\mathbf{a}}$ (with all possible $\mathbf{a}$) that satisfy the equations

$$T_{\mathbf{a}}\Phi_{\mathbf{k}} = e^{i\mathbf{k}\mathbf{a}}\Phi_{\mathbf{k}}. \quad (4)$$

It is well known that the total momentum of the system is represented by the operator $\mathbf{P} = -i\hbar(\nabla_{\mathbf{a}} T_{\mathbf{a}})_{\mathbf{a}=0}$. The $\Phi_{\mathbf{k}}$ are then eigenfunctions of this operator belonging to the eigenvalues $\hbar\mathbf{k}$.

The trial functions we choose for this system are

$$\Phi_{\mathbf{k}} = A\int \exp\{-i\mathbf{k}\xi\}\, T_\xi \Psi\,(d\xi), \tag{5}$$

$$\Psi = (2\beta/\pi)^{3/4} \exp\Big\{-\beta r^2 - \frac{1}{2}\sum_\varkappa \Big(x_\varkappa^2 + \frac{1}{2}\ln\pi\Big)\Big\},\quad x_\varkappa = q'_\varkappa + s_\varkappa,\quad q'_\varkappa = q_\varkappa - a_\varkappa \chi_{-\varkappa}(\mathbf{r}). \tag{6}$$

The form of (6) is taken from our previous work,[1] and the a_κ, s_κ, and β are to be the variation parameters. For arbitrary real $\mathbf{k}$ the function of Eq. (5) is an exact simultaneous eigenfuction of $T_{\mathbf{a}}$ and $\mathbf{P}$. Since the $\Phi_{\mathbf{k}}$ with different $\mathbf{k}$ belong to different momentum eigenvalues, they are mutually orthogonal.

According to the variational method in quantum mechanics, we must obtain an extremum of the functional

$$\overline{\overline{H}} = \int \Phi_{\mathbf{k}}^* H \Phi_{\mathbf{k}} d\tau,$$

with the subsidiary condition $\int \Phi_{\mathbf{k}}^*\Phi_{\mathbf{k}} d\tau = 1$. It is easily shown that

$$\overline{\overline{H}} = AA^*\int d\tau \iint \exp\{i\mathbf{k}(\xi_1 - \xi_2)\}(d\xi_1)(d\xi_2)\, T_{\xi_1}\Psi^* H T_{\xi_2}\Psi = AA^* V\int d\tau \int \exp\{i\mathbf{k}\xi\}\, T_\xi \Psi^* H\Psi\,(d\xi). \tag{7}$$

This is done by applying $T_{-\xi_2}$ to the whole integrand in (7) (this does not change the value of the integral) and making use of the invariance of H under translation. The normalizing integral can be similarly transformed.

After changing from the variables $\mathbf{r}, \ldots, q_\kappa, \ldots$ to the new variables $\mathbf{r}, \ldots, q'_\kappa, \ldots$ the Hamiltonian can be written in the form

$$\begin{gathered} H = \sum_{l=1}^{8} I_l,\quad I_1 = -\frac{\hbar^2}{2m}\Delta,\quad I_2 = \frac{\hbar^2}{m}\sum_\varkappa (\nabla q_{\varkappa 0}, \nabla)\frac{\partial}{\partial q'_\varkappa},\quad I_3 = -\frac{\hbar^2}{2m}\sum_{\varkappa,\varkappa_1}(\nabla q_{\varkappa 0}\cdot\nabla q_{\varkappa_1 0})\frac{\partial^2}{\partial q'_\varkappa \partial q'_{\varkappa_1}},\quad I_4 = \frac{\hbar^2}{2m}\sum_\varkappa \Delta q_{\varkappa 0}\frac{\partial}{\partial q'_\varkappa}, \\ I_5 = \frac{1}{2}\sum_\varkappa \hbar\omega_\varkappa q'^2_\varkappa,\quad I_6 = \sum_\varkappa (\hbar\omega_\varkappa a_\varkappa + c_\varkappa)\, q'_\varkappa \chi_{-\varkappa}(\mathbf{r}),\quad I_7 = \sum_\varkappa \Big(\frac{1}{2}\hbar\omega_\varkappa a_\varkappa^2 + c_\varkappa a_\varkappa\Big)\chi^2_{-\varkappa}(\mathbf{r}),\quad I_8 = -\frac{1}{2}\sum_\varkappa \hbar\omega_\varkappa \frac{\partial^2}{\partial q'^2_\varkappa}. \end{gathered} \tag{8}$$

The value of the Jacobian of the transformation indicated in (7) is just unity. The integration over the new variables can be performed exactly. We introduce the notation

$$\overline{\overline{f}} = \frac{1}{I}\int \exp\Big\{-\sum_\varkappa \frac{s_\varkappa^2}{2}(1 - \cos\varkappa\xi) - \frac{\beta\xi^2}{2}\Big\} f(\xi)\cos\mathbf{k}\xi\,(d\xi), \tag{9}$$

where

$$I = \int \exp\Big\{-\sum_\varkappa \frac{s_\varkappa^2}{2}(1 - \cos\varkappa\xi) - \frac{\beta\xi^2}{2}\Big\}\cos\mathbf{k}\xi\,(d\xi), \tag{10}$$

and then the result can be written

$$\begin{gathered} \overline{\overline{H}} = \sum_{l=1}^{8}\overline{\overline{I}}_l,\quad \overline{\overline{I}}_1 = \frac{3\hbar^2\beta}{2m} - \frac{\hbar^2\beta^2}{2m}\overline{\overline{\xi^2}},\quad \overline{\overline{I}}_2 = -\frac{\hbar^2\beta}{m\sqrt{V}}\sum_\varkappa a_\varkappa s_\varkappa e^{-\varkappa^2/8\beta}\,\overline{\overline{(\varkappa\xi)\sin(\varkappa\xi/2)}}, \\ \overline{\overline{I}}_3 = \frac{\hbar^2}{4mV}\sum_\varkappa a_\varkappa^2\varkappa^2 - \frac{\hbar^2}{2mV}\sum_{\varkappa,\varkappa_1} a_\varkappa a_{\varkappa_1} s_\varkappa s_{\varkappa_1}(\varkappa\varkappa_1)\, e^{-(\varkappa-\varkappa_1)^2/8\beta}\,\overline{\overline{\sin(\varkappa\xi/2)\sin(\varkappa_1\xi/2)}}, \\ \overline{\overline{I}}_4 = 0,\quad \overline{\overline{I}}_5 = \frac{1}{4}\sum_\varkappa \hbar\omega_\varkappa(1 + s_\varkappa^2) + \frac{1}{4}\sum_\varkappa \hbar\omega_\varkappa s_\varkappa^2\overline{\overline{\cos\varkappa\xi}},\quad \overline{\overline{I}}_6 = -V^{-1/2}\sum_\varkappa (\hbar\omega_\varkappa a_\varkappa + c_\varkappa)\, s_\varkappa e^{-\varkappa^2/8\beta}\,\overline{\overline{\cos(\varkappa\xi/2)}}, \\ \overline{\overline{I}}_7 = \frac{1}{V}\sum_\varkappa\Big(\frac{1}{2}\hbar\omega_\varkappa a_\varkappa^2 + c_\varkappa a_\varkappa\Big),\quad \overline{\overline{I}}_8 = \frac{1}{4}\sum_\varkappa \hbar\omega_\varkappa(1 - s_\varkappa^2) + \frac{1}{4}\sum_\varkappa \hbar\omega_\varkappa s_\varkappa^2\overline{\overline{\cos\varkappa\xi}}. \end{gathered} \tag{11}$$

In obtaining (11), the a_κ and s_κ are restricted by $a_\kappa = a_{-\kappa}$ and $s_\kappa = s_{-\kappa}$. For the a_κ and s_κ we shall use, for simplicity, expressions previously obtained[1] by minimizing $\overline{\overline{H}}$ in the approximation without translational symmetry, namely

$$a_\varkappa = -\frac{c_\varkappa(1 - e^{-\varkappa^2/4\beta})}{(\hbar^2\varkappa^2/2m) + \hbar\omega_\varkappa(1 - e^{-\varkappa^2/4\beta})},\quad s_\varkappa = \Big(a_\varkappa + \frac{c_\varkappa}{\hbar\omega_\varkappa}\Big)V^{-1/2}e^{-\varkappa^2/8\beta}. \tag{12}$$

Somewhat more exact but more complicated results could have been obtained by determining the a_κ and

s_κ from the extremum condition of the functional $\overline{\overline{H}}$ given by (11).

It follows from (11) and (12) that

$$\overline{\overline{H}} = \sum_{\varkappa} \frac{1}{2} \hbar\omega_\varkappa + \frac{3\hbar^2\beta}{2m} - \frac{1}{2V} \sum_{\varkappa} \frac{c_\varkappa^2}{\hbar\omega_\varkappa} e^{-\varkappa^2/4\beta} - \frac{1}{2V} \sum_{\varkappa} \frac{c_\varkappa^2 (1 - e^{-\varkappa^2/4\beta})^2}{(\hbar^2\varkappa^2/2m) + \hbar\omega_\varkappa (1 - e^{-\varkappa^2/4\beta})}$$

$$- \frac{\hbar^2\beta^2}{2m} \overline{\xi^2} - \frac{\hbar^2\beta}{mV\overline{V}} \sum_{\varkappa} a_\varkappa s_\varkappa e^{-\varkappa^2/8\beta} \overline{(\varkappa\xi) \sin (\varkappa\xi/2)} + \sum_{\varkappa} \frac{1}{2} \hbar\omega_\varkappa s_\varkappa^2 \left[\overline{\cos (\varkappa\xi)} - 2\overline{\cos (\varkappa\xi/2)}\right] \tag{13}$$

$$+ \sum_{\varkappa} \frac{1}{2} \hbar\omega_\varkappa s_\varkappa^2 - \frac{\hbar^2}{2mV} \sum_{\varkappa, \varkappa_1} a_\varkappa a_{\varkappa_1} s_\varkappa s_{\varkappa_1} (\varkappa\varkappa_1) e^{-(\varkappa-\varkappa_1)^2/8\beta} \overline{\sin (\varkappa\xi/2) \sin (\varkappa_1\xi/2)}.$$

Here the first four terms agree with the previously obtained expression for $\overline{\overline{H}}$ in the absence of the additional external field $V(\mathbf{r})$. The remaining terms in (13) arise as a result of the transition to translational symmetry in the trial functions of (5) and (6). These are the only terms which depend on the momentum of the system.

2. DEPENDENCE OF THE ENERGY ON THE MOMENTUM AND ENERGY OF THE POLARON GROUND STATE

In an attempt to make the problem more specific and to perform some numerical calculations, let us henceforth consider the particular case of a polaron when there is no dispersion of the optical lattice vibrations ($\omega_\kappa = \omega$). In this case we have

$$c_\varkappa = -e \sqrt{4\pi\hbar\omega_\varkappa c} / |\varkappa| \quad c = 1/n^2 - 1/\varepsilon. \tag{14}$$

Here ϵ is the static dielectric constant of the crystal, n is the index of refraction, and e is the electron charge. In Eq. (1) m is the effective mass of a band electron.

Let us first consider the limiting case of strong coupling between the electron and polar crystal vibrations, that is the case of large c. We replace $\mathbf{k}$ and c by the dimensionless wave vector $\mathbf{k}'$ and the dimensionless coupling constant α given by

$$\mathrm{k}' = -\frac{\mathrm{k}}{e} \left(\frac{3\pi^{1/2}\hbar\omega}{c\beta_0^{3/2}}\right)^{1/2}, \quad \beta_0 = \frac{m^2e^4c^2}{9\pi\hbar^4}, \quad \alpha = \frac{e^2c}{\hbar^{3/2}} \left(\frac{m}{2\omega}\right)^{1/2}. \tag{15}$$

Let us now expand $\overline{\overline{H}}$ as given by (13) in a power series in $\mathbf{k}$, retaining terms of order $\mathbf{k}^0$, $\mathbf{k}^2$, and $\mathbf{k}^4$. We then expand each coefficient of this series in inverse powers of α, retaining terms of order α^2, α^0, and α^{-2}. To do this we expand the trigonometric functions of $(\kappa\xi)$ in the last four terms of the integrand of (13) in powers of $(\kappa\xi)$ up to terms of order $(\kappa\xi)^4$ inclusive. The result so obtained can be simplified by averaging over angles in κ-space, which leads to

$$\overline{\overline{H}} = R(\beta) + \overline{\xi^2} \Big[-\frac{\hbar^2\beta^2}{2m} - \frac{\hbar^2\beta}{6mV\overline{V}} \sum_{\varkappa} a_\varkappa s_\varkappa e^{-\varkappa^2/8\beta} \varkappa^2 - \frac{\hbar\omega}{24} \sum_{\varkappa} s_\varkappa^2 \varkappa^2 - \frac{\hbar^2}{24mV} \sum_{\substack{n=0 \\ (n\text{ — even})}}^{\infty} \frac{1}{(n+3)\, n!} \Big(\sum_{\varkappa} a_\varkappa s_\varkappa e^{-\varkappa^2/8\beta} y^n \varkappa^2 \Big)^2 \Big]$$

$$+ \overline{\xi^4} \Big[\frac{\hbar^2\beta}{240mV\overline{V}} \sum_{\varkappa} a_\varkappa s_\varkappa e^{-\varkappa^2/8\beta} \varkappa^4 + \frac{7\hbar\omega}{1920} \sum_{\varkappa} s_\varkappa^2 \varkappa^4 + \frac{\hbar^2}{480mV} \sum_{n=0}^{\infty} \frac{1}{n!\,(n+3)} \sum_{\varkappa} a_{\varkappa_1} s_\varkappa e^{-\varkappa^2/8\beta} y^n \varkappa^4 \sum_{\varkappa_1} a_{\varkappa_1} s_{\varkappa_1} e^{-\varkappa_1^2/8\beta} y_1^n \varkappa_1^2 \Big], \tag{16}$$

$$y = \varkappa / 2\sqrt{\beta}, \quad y_1 = \varkappa_1 / 2\sqrt{\beta}.$$

Here $R(\beta)$ is the sum of the first four terms of (13). It is now necessary to calculate $\overline{\xi^2}$ and $\overline{\xi^4}$ with the required accuracy. This is done by expanding the arguments of the exponential in (9) and (10) in powers of $(\kappa\xi)$, leaving the term of order $(\kappa\xi)^2$ in the exponent, and writing the exponential containing higher powers of $(\kappa\xi)$ in the form of a series. We then obtain

$$\overline{\xi^2} = \delta^{-1} \Big[\frac{3}{2} + \frac{15}{2} \gamma\delta^{-2} + k^2 \Big(-\frac{1}{4} \delta^{-1} - \frac{15}{4} \gamma\delta^{-3} \Big) + \frac{1}{4} k^4 \gamma\delta^{-4} \Big]; \quad \overline{\xi^4} = \delta^{-2} \Big[\frac{15}{4} - \frac{5}{4} \delta^{-1} k^2 + \frac{1}{16} \delta^{-2} k^4 \Big], \tag{17}$$

where

$$\delta = \frac{1}{12} \sum_{\varkappa} s_\varkappa^2 \varkappa^2 + \frac{1}{2} \beta, \quad \gamma = \frac{1}{240} \sum_{\varkappa} s_\varkappa^2 \varkappa^4.$$

If we now calculate all the sums over κ by replacing them by integrals in κ-space, then (16) leads to

$$\frac{\overline{\overline{H}}}{\hbar\omega} = \sum_{\varkappa}\frac{1}{2} + \frac{\alpha^2}{3\pi}(\zeta - 2\zeta^{1/2}) - 3(2-\sqrt{2})\zeta^{-1/2} + \frac{27\pi\cdot 0.096}{2\alpha^2} + \left[\frac{3}{2} + \frac{81\pi}{8\alpha^2} + k'^2\left(-\frac{1}{4}\zeta^{-3/2} - \frac{9\pi\cdot 2.29}{4\alpha^2}\right) + k'^4\frac{27\pi}{80\alpha^2}\right]$$
$$\times\left(1 + \frac{9\pi}{\alpha^2}0.043\right)\left[-\frac{1}{2}\zeta^{1/2} + 0.086 - 0.235\zeta^{-1/2} + \frac{9\pi}{\alpha^2}0.098\right] + \frac{9\pi}{5\alpha^2}0.649\left[\frac{15}{4} - \frac{5}{4}k'^2 + \frac{1}{16}k'^4\right], \quad \zeta = \beta/\beta_0. \tag{18}$$

The value of ζ is found from the condition that $\overline{\overline{H}}$ be a minimum. The expansion of ζ in powers of α is of the form

$$\zeta = 1 + 6\pi\alpha^{-2}(-0.68 + 0.21\,k'^2). \tag{19}$$

Inserting (19) into (18) we obtain

$$\frac{\overline{\overline{H}}}{\hbar\omega} = -\frac{1}{3\pi}\alpha^2 - 2.73 - \frac{8.6}{\alpha^2} + k'^2\left[0.16 + \frac{10.8}{\alpha^2}\right] - k'^4\frac{1.28}{\alpha^2}, \tag{20}$$

$$\overline{\overline{H}} = -\left(0.106\alpha^2 + 2.73 + \frac{8.6}{\alpha^2}\right)\hbar\omega + \frac{P^2}{2M} + \frac{P^4}{2N}, \quad M = 155\left(\frac{\alpha}{10}\right)^4\left[1 + \frac{67}{\alpha^2}\right]^{-1} m, \qquad N = -9.7\cdot 10^4\left(\frac{\alpha}{10}\right)^{10} m^2\hbar\omega. \tag{21}$$

In the limiting case of weak coupling Eq. (13) leads quite simply to the first terms in the series for the ground state energy and effective mass by setting $s_K = 0$ and

$$a_\varkappa = -c_\varkappa/[(\hbar^2\varkappa^2/2m) + \hbar\omega(1 - e^{-\varkappa^2/4\beta})]$$

(these are the asymptotic values of the s_K and the a_K as given by (12) in the limit as $c \to 0$). The result $\overline{\overline{H}} = -\alpha\hbar\omega + P^2/2m$ coincides with the exact one. We have not calculated further terms in the series. Allcock[3] summarizes the results of various authors' calculations of the polaron ground state energy and effective mass. Comparison of these results shows that in the intermediate-coupling region ($\alpha \sim 5$) Feynman[2] obtains the most accurate result. Expression (20) obtained here gives a somewhat lower ground state energy for $\alpha = 5$ (at least by 7% if the term of order c^{-2} in Feynman's expression for the energy is positive, as he himself supposes).

The convergence of the power series in $1/\alpha^2$ for the ground state energy is much better than that of the analogous series for the effective mass. It is therefore desirable to obtain the subsequent terms in the power series in α^{-2} for the effective mass for real ionic crystals ($\alpha \sim 8$).

Nevertheless, let us give the effective mass of the polaron in NaCl as calculated according to (21). This is $M = 49$ m (if we assume[4] that $\alpha^2 = 77$ in NaCl). The Feynman-Allcock formula[4] (the first two terms in Feynman's expansion) gives $M = 40.8$ m in this case. For a polaron kinetic energy equal to about $\hbar\omega$ in NaCl, the $P^4/2N$ term is about 20% of the $P^2/2M$ term.

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