Some Contributions to Polaron Theory

A. E. K. Dowson * and D. ter Haar

Department of Theoretical Physics, 12 Parks Road, Oxford, Great Britain

(Z. Naturforschg. **22 a**, 1300—1303 [1967]; received 29 May 1967)

Dedicated to Professor Pascual Jordan *on the occasion of his 65th birthday*

We give a microscopic derivation of the single-phonon electron-lattice interaction in an ionic crystal usually employed in polaron theory. We then examine the nature of the coupling with the acoustic lattice modes and, for a simple, one-dimensional model, find conditions under which discontinuous changes in the binding energy of an acouston may occur.

There exists an extensive literature on polaron theory. The early work can be found in Pekar's monograph [1], while Schultz's MIT thesis [2] gives the literature up to 1956. (We refer also to Kittel's recent text-book [3]). In this theory one uses an interaction describing the effect of the lattice on the motion of an electron in an ionic crystal. The expression for this interaction is usually derived phenomenologically [1–5], but in the present paper we shall for a simplified model derive it microscopically, using a definition of the dielectric constant due to Nozières and Pines [6]. In this way we are able to indicate some of the assumptions underlying the application of the usual expression.

Our treatment also reveals a short-range interaction with the acoustic lattice modes which is lost in the normal continuum model, and we shall study what light this sheds on the possible existence of a self-trapped acouston.

1. The Electron-Lattice Interaction

The model we are using is that of an ionic lattice of bare point charges. If an extra electron is placed in the lattice at $\boldsymbol{R}$, the interaction $V_0(\boldsymbol{R})$ with the undisplaced ions will be

$$V_0(\boldsymbol{R}) = -\sum_j e\,Z_j / |\,\boldsymbol{R} - \boldsymbol{s}_{0j}\,|\,, \tag{1}$$

where $e\,Z_j$ is the charge of the j-th ion and $\boldsymbol{s}_{0j}$ its equilibrium position. If now the ions are slightly displaced from their equilibrium, by $\delta\boldsymbol{s}_j$ say, the interaction becomes

$$V = V_0 + V_{\text{int}}(\boldsymbol{R}), \tag{2}$$

where

$$\begin{aligned} V_{\text{int}}(\boldsymbol{R}) &= \sum_j (\delta\boldsymbol{s}_j \cdot \nabla_j V_0) \\ &= -\sum_j \frac{e\,Z_j}{(\boldsymbol{R} - \boldsymbol{s}_{0j})^2}\,(\boldsymbol{R} - \boldsymbol{s}_{0j} \cdot \delta\boldsymbol{s}_j)\,. \end{aligned} \tag{3}$$

The displacement $\delta\boldsymbol{s}_j$ can be expanded in terms of creation and annihilation operators as follows [3, 7]

$$\begin{aligned} \delta\boldsymbol{s}_j \equiv \delta\boldsymbol{s}_{\boldsymbol{n},\boldsymbol{b}} = &-i \sum_{p,q} \boldsymbol{e}_{qbp} \\ &\times \beta_{qbp} [a_{qp}^{+} \exp\{-i\,\boldsymbol{q}\cdot\boldsymbol{n}\} - a_{qp} \exp\{i\,\boldsymbol{q}\cdot\boldsymbol{n}\}]\,, \end{aligned} \tag{4}$$

where we have characterized the j-th ion by two vectors, $\boldsymbol{b}$ and $\boldsymbol{n}$, with $\boldsymbol{n}$ a lattice vector and $\boldsymbol{b}$ the basis vector of the appropriate ion in the unit cell, where the $\boldsymbol{e}_{qbp}$ are polarisation vectors, and the β_{qbp} normalization constants (we normalize to unit volume):

$$\beta_{qbp} = [\pi\,\hbar / m_b\,\omega_{qp}]^{1/2}. \tag{5}$$

Here q is the wave-vector of the relevant mode, p indicates the branch, and ω_{qp} the frequency of the q, p-th mode.

Substituting (4) into (3), we see that we are left with a sum over p, q, $\boldsymbol{n}$ and $\boldsymbol{b}$. The summation over $\boldsymbol{n}$ can be performed by using for the R-dependent part the identity, valid for any function $G(\boldsymbol{R})$:

$$\begin{aligned} G(\boldsymbol{R}) = \sum_{\boldsymbol{k}} [\,\int \mathrm{d}^3\boldsymbol{R}'\,G(\boldsymbol{R}')\exp\{i\,\boldsymbol{k}\cdot\boldsymbol{R}'\}] \\ \cdot \exp\{-i\,\boldsymbol{k}\cdot\boldsymbol{R}\}\,, \end{aligned} \tag{6}$$

---

* Present address: Department of Mathematics, Imperial College, London, S.W. 7.

[1] S. I. Pekar, Research in Electron Theory of Crystals, Moscow 1951; English version published in 1963 by the USAEC, No. AEC-tr-5575.

[2] T. D. Schultz, Solid State and Molecular Theory Group, MIT, Technical Report No. 9, 1956.

[3] C. Kittel, Quantum Theory of Solids, J. Wiley, New York 1963.

[4] G. R. Allcock, Advan. Phys. **5**, 412 [1956].

[5] H. Fröhlich, Advan. Phys. **3**, 325 [1954].

[6] P. Nozières and D. Pines, Nuovo Cimento **9**, 470 [1958].

[7] A. S. Davydov, Quantum Mechanics, Pergamon Press, Oxford 1965, Chap. XIII.

where the sum is over the first BRILLOUIN zone. The integration over $\boldsymbol{R}'$ can thus performed, and the summation over $\boldsymbol{n}$ leads to a δ-function which allows us to sum over $\boldsymbol{k}$. The final result is:

$$V_{\text{int}}(\boldsymbol{R}) = 4\pi i e \sum_{q,p} (1/|\boldsymbol{q}|) \cdot [F(q,p)\, a_{qp}^{+} \exp\{-i\,\boldsymbol{q}\cdot\boldsymbol{R}\} - \text{h.c.}] \,, \tag{7}$$

where the structure factor $F(q,p)$ is

$$F(q,p) = \sum_{b} [\pi\hbar/m_b\,\omega_{qp}]^{1/2} Z_b\, |\boldsymbol{q}|^{-1} (\boldsymbol{q}\cdot\boldsymbol{e}_{qbp}) \exp\{i\,\boldsymbol{q}\cdot\boldsymbol{b}\}\,. \tag{8}$$

Instead of a coupling involving the bulk properties of the crystal, we find a quantity involving only one unit cell. This factor will in general show a marked $\boldsymbol{q}$-dependence, which we may expect to reduce the coupling with wave-vectors close to the edge of the BRILLOUIN zone. Thus the interaction drops off even faster than the $1/q$ decrease of the usual macroscopic formula[1–3].

For optical modes, $\boldsymbol{e}_{qbp}$ changes sign for some values of $\boldsymbol{b}$, and the coupling will obviously be strongest for those modes where $\boldsymbol{e}_{qbp}$ changes sign at the same sites as Z_b. This gives us a criterion for estimating the strength of the interaction with a given mode.

For acoustic modes, $\boldsymbol{e}_{qbp}$ does not change sign for any $\boldsymbol{b}$, and hence the coupling will be small if there is over-all charge neutrality in each cell. However, $F(q,p)$ will not vanish for all $\boldsymbol{q}$, and in this case we expect the phasefactor $\exp\{i\,\boldsymbol{q}\cdot\boldsymbol{b}\}$ to tend to increase the coupling for large values of $\boldsymbol{q}$.

From this discussion it is clear that the microscopic formula (7) contains a wealth of detailed information on the coupling of each specific lattice mode with a given electron. This is in contrast to the macroscopic formula, which must in some sense be an average interaction taken over all (optical) modes.

2. Connection with the Dielectric Constant

We now wish to establish under what conditions Eq. (7) reduces to the usual macroscopic formula, where we have[3]

$$V_{\text{int}}(\boldsymbol{R}) = \sum_{q} v_q\, a_q^{+} \exp\{-i\,\boldsymbol{q}\cdot\boldsymbol{R}\} + \text{h.c.}, \tag{9}$$

with

$$v_q^2 = 2\pi e^2 \hbar\omega\, [1/\varepsilon_\infty - 1/\varepsilon_0]\,, \tag{10}$$

where ε_∞ and ε_0 are, respectively, the square of the optical refractive index and the static dielectric constant.

To find a connection between (9) and (7) we must define the dielectric constant in microscopic terms. We do this by using the definition of NOZIÈRES and PINES[6]:

$$1/\varepsilon_q = 1 + \langle\varrho_q\rangle/\eta_q\,, \tag{11}$$

where $\langle\varrho_q\rangle$ is the thermal average of the q-th FOURIER component of the charge density fluctuation due to a (weak) test charge η_q.

The charge density $\varrho(\boldsymbol{r})$ is clearly given by the expression

$$\varrho(\boldsymbol{r}) = e \sum_{n,b} Z_b\, \delta(\boldsymbol{r} - \boldsymbol{n} - \boldsymbol{b} - \delta\boldsymbol{s}_{n,b})\,. \tag{12}$$

Substituting (4) into (1), FOURIER transforming, assuming $\delta\boldsymbol{s}_{n,b}$ to be sufficiently small that we may expand $\exp\{i(\boldsymbol{q}\cdot\delta\boldsymbol{s}_{n,b})\}$ in powers of $\boldsymbol{q}$ and retaining only the first non-vanishing term after using the charge neutrality condition, summing over $\boldsymbol{n}$ and noting that $\boldsymbol{e}_{qbp}$ and β_{qbp} are, respectively, odd and even functions of $\boldsymbol{q}$, we get:

$$\varrho_q = -e \sum_{b,p,q} Z_b (\boldsymbol{q}\cdot\boldsymbol{e}_{qbp})\, \beta_{qbp} \exp\{i\,\boldsymbol{q}\cdot\boldsymbol{b}\}\, (a_{qp}^{+} + a_{qp})\,. \tag{13}$$

To find $\langle\varrho_q\rangle$ we use perturbation theory. As long as the temperature T satisfies the inequality

$$k_{\text{Bo}}\, T \lesssim \hbar\,\omega_{\text{opt}}$$

we can take the unperturbed state of the lattice to be the ground state. This inequality is not very restrictive as the excitation energy $\hbar\,\omega_{\text{opt}}$ of the optical lattice modes is quite high.

The perturbation due to the insertion of the test charge will be

$$V_{\text{pert}} = (4\pi/q^2)\,(\eta_q\,\varrho_q + \text{h.c.})\,, \tag{14}$$

and using the perturbation expression for the perturbed ground state wave-function – which contains an admixture of unperturbed one-phonon states – and expression (13) for ϱ_q, we find after some straightforward calculation that to this order the non-vanishing terms lead to

$$\langle\varrho_q\rangle = -\sum_{p} (2\,\eta_q/\hbar\,\omega_{qp}\,q^2) \cdot \Big|\sum_{b} Z_b (\boldsymbol{q}\cdot\boldsymbol{e}_{qbp})\, \beta_{qbp} \exp\{i\,\boldsymbol{q}\cdot\boldsymbol{b}\}\Big|^2, \tag{15}$$

or, from (11) and (8),

$$\frac{1}{8\pi}\left(\frac{1}{\varepsilon_q} - 1\right) = -\sum_{p} \frac{F(q,p)\,F^*(q,p)}{\hbar\,\omega_{qp}}\,. \tag{16}$$

In the limit as $q \to 0$ – a limit effectively taken at the start of the usual derivation – assuming that the coupling does not vary much from its $q = 0$

value and that only the optical branches need be considered, we can make the identification

$$F(q,p) = F^*(q,p) = \left[\frac{\hbar\,\omega_{qp}}{8\pi}\left(1-\frac{1}{\varepsilon_{qp}}\right)\right]^{1/2} \approx \left[\frac{\hbar\,\omega_0}{8\pi}\left(1-\frac{1}{\varepsilon_0}\right)\right]^{1/2}, \tag{17}$$

and the interaction becomes

$$V_{\text{int}}(\boldsymbol{R}) = i\,e\left[2\pi\hbar\,\omega_0\left(1-\frac{1}{\varepsilon_0}\right)\right]^{1/2} \cdot \sum_q \frac{1}{|\boldsymbol{q}|}\,(a_q^+ \exp\{-i\,\boldsymbol{q}\cdot\boldsymbol{R}\} - \text{h. c.}), \tag{18}$$

which is identical with (9) for our bare point-charge model in which $\varepsilon_\infty = 1$.

3. Interaction with Acoustic Modes

The expression (7) is exact in the limit of small lattice displacements, and we can use it to consider the interaction of an electron with the acoustic modes. In that case, the coupling has a short range, would vanish in the limit as $q \to 0$, and is therefore lost in the continuum approximation.

To study this case we consider the very simple model of a linear chain of alternately possive and negative ions of equal mass M and a distance a apart. The dispersion relation for the acoustic mode is then [8]:

$$\omega_q^2 = \frac{4\pi^2 g}{M}\,(1-\cos q\,a), \tag{19}$$

where g is a coupling constant. In this case (7) has the form (9) with

$$|v_q^2| = \frac{8\pi^2 e^2 Z^2 \hbar}{2\,M a}\,(2\,M/g)^{1/2}\,\frac{\tan(q\,a/4)}{q^2}\,. \tag{20}$$

We remark that an analysis based on (20) would seem to be about as valid as optical polaron theory, as both that theory and (20) stem from (7). However, Toyozawa [9], in studying the so-called "acouston" – an electron clothed by acoustic phonons – worked with the deformation potential, which is of even shorter range than (20), having $|v_q^2| \sim q$ for small q. This potential was originally derived [10] on the assumption that the ionic potential is screened out over distances greater than the dimensions of the unit cell by cooperative effects due to the other electrons. This assumption is clearly appropriate to the case of a metal, but is not so obviously applicable to ionic crystals, where the number of screening electrons is so much smaller. We shall therefore examine some of the consequences of (20). Especially interesting is the possibility of "self-trapping" – a discontinuous change in the self-energy and effective mass of the acouston as the coupling parameter is varied. Although Toyozawa [9] claims to have shown that self-trapping occurs, his wave-function was to some extent selected arbitrarily to promote a discontinuity.

4. The Acouston Self-Energy

Assuming the relevance of Pekar's adiabatic theory [1], we have, for the self-energy of our quasiparticle,

$$E[\psi] = \underset{\psi}{\text{Min}}\left[\left\langle\frac{p^2}{2\,m}\right\rangle - \sum_q \frac{|v_q|^2}{\hbar\,\omega_q}\,|\langle\exp\{i\,\boldsymbol{q}\cdot\boldsymbol{R}\}\rangle|^2\right], \tag{21}$$

where $\langle\ldots\rangle$ indicates an average with respect to the wave-function $\psi(\boldsymbol{r})$, and where the self-energy is obtained by minimising $E[\psi]$ as a functional of $\psi(\boldsymbol{r})$.

The Euler–Lagrange equation resulting from (21) is non-linear, and in view of the computational complications we have only considered one set of trial functions, to wit Gaussian functions. We then find – after some simplifications which we hope do not affect the qualitative result – that although the variation in $E_{\min}$ becomes steep for a wave-function with a scale of the order of the lattice spacing, there is no discontinuity in $E_{\min}$ such as was found by Toyozawa. We have not yet considered two-parameter wave-functions such as those describing the eigenstates of a particle in a potential well of variable height and width, but it does not seem likely that such a modification would greatly influence this conclusion.

5. Discontinuities in the Presence of a Shielded Potential

An interesting question is whether our approach can reveal discontinuities in $E_{\min}$ when a certain

---

[8] See, for instance, D. ter Haar, Elements of Hamiltonian Mechanics, North-Holland Publ. Co., Amsterdam 1964, § 3.4.

[9] Y. Toyozawa, Prog. Theor. Phys. **26**, 1 [1961].

[10] J. Bardeen and W. Shockley, Phys. Rev. **80**, 72 [1950].

amount of shielding is introduced into the ionic potential. This can be achieved by changing the denominator q^2 in (20) to $q^2+\Delta^2$.

Substituting this new expression for v_q into (21), and using the GAUSSian trial function

$$\psi(r) = (\beta/\pi)^{3/4}\, e^{-\beta r^2/2}, \tag{22}$$

we find, after assuming Δ^2/β to be a small quantity and that the main contributions to $E(\beta)$ come from the region of small q,

$$E'_{\min} = \tfrac{1}{2}\pi\Delta - \tfrac{1}{8}\pi\,\alpha^2, \tag{23}$$

where

$$E' = \frac{E}{3\,\hbar^2/4\,m\,a^2}, \qquad \alpha = \frac{4\,m\,e^2\,Z^2}{3\,g\,\hbar^2\,a^2}\,\frac{m}{M}. \tag{24}$$

From this we see that a discontinuity in the self-energy may occur if Δ is sufficiently small.

Our conclusion is tentative, but the analysis shows that self-trapping is critically dependent on the amount of screening involved.

Acknowledgements

We express thanks to the D.S.I.R. (now the S.R.C.) for a maintenance grant to one of us (AEKD) during the tenure of which this work was carried out.

Hauptsätze über das Messen als Grundlage der Hilbert-Raumstruktur der Quantenmechanik

GÜNTHER LUDWIG

Institut für Theoretische Physik der Universität Marburg

(Z. Naturforschg. **22 a**, 1303—1323 [1967]; eingegangen am 24. Mai 1967)

Herrn Professor Dr. PASCUAL JORDAN *zum 65. Geburtstag gewidmet*

Ähnlich wie bei den Hauptsätzen der Thermodynamik werden heuristische Gesichtspunkte diskutiert, die zur Aufstellung von allgemeinen Hauptsätzen über die Wirkung von Mikroobjekten auf makroskopische (d. h. dem thermodynamischen Gesetz der Entropiezunahme genügenden) Systeme führen. Das Ziel ist, durch solche allgemeinen „Hauptsätze des Messens“ die Struktur des HILBERT-Raumes der Quantenmechanik zu charakterisieren. Die hier angegebenen Hauptsätze (Axiome 1 bis 3) führen zwar zu mathematischen Strukturen, die sehr viel von den Strukturen des HILBERT-Raumes enthalten, aber noch allgemeiner als der HILBERT-Raum sein können. Vielleicht enthalten sie neue interessante Möglichkeiten für neue physikalische Theorien.

I. Grundbegriffe

Die Quantenmechanik ist durch eine merkwürdige „Grundstruktur“ charakterisiert, den HILBERT-Raum. Deshalb ließ es schon gleich zu Beginn vielen Physikern keine Ruhe, ein tieferes Verständnis für diese Grundstruktur zu gewinnen[1]. Trotz mancher Teilerfolge[1, 2] erwiesen sich aber alle bisherigen Versuche als entweder physikalisch nicht ganz durchschaubar oder konnten das Ziel, den HILBERT-Raum zu charakterisieren, nicht voll erreichen. Wir wollen hier versuchen, auf jeden Fall physikalisch interpretierbare Sätze als Ausgangspunkt der Theorie zu benutzen; aber auch wir werden nicht ganz das Endziel, eine *vollständige* Charakterisierung des HILBERT-Raumes, erreichen. Vielleicht aber sollte man hierüber nicht unzufrieden sein, falls man hierbei andere interessante Basistrukturen für physikalische Theo-

---

[1] W. HEISENBERG, Z. Physik **43**, 172 [1927]. — N. BOHR, Naturwiss. **16**, 245 [1928]. — W. HEISENBERG, Die physikalischen Prinzipien der Quantentheorie, Hirzel, Berlin 1930. — G. BIRKHOFF u. J. v. NEUMANN, Ann. Math. **37**, 823 [1936]. — P. JORDAN, Anschauliche Quantentheorie, Springer, Berlin 1936. — I. E. SEGAL, Ann. Math. **48**, 930 [1947].

[2] D. BOHM, Phys. Rev. **85**, 166 [1952]. — P. JORDAN, Z. Physik **133**, 21 [1952]. — G. W. MACKEY, Amer. Math. Monthly **64**, No. 8 (II) 45 [1957]. — N. ZIERLER, Pac. J. Math. **11**, 1151 [1961]. — G. EMCH u. C. PIRON, J. Math. Phys. **4**, 469 [1963]. — G. EMCH, Helv. Phys. Acta **36**, 739 [1963]. — J M. JAUCH u. C. PIRON, Helv. Phys. Acta **36**, 827 [1963]. — C. PIRON, Helv. Phys. Acta **37**, 439 [1964]. — G. LUDWIG, Z. Physik **181**, 233 [1964]. — M. D. MACLAREN, ANL 7065 Argonne National Laboratory, Argonne, Illinois 1965. — I. AMEMIYA u. H. ARAKI, Research Inst. Math. Sci. RIMS-12 [1966], Kyoto, Japan. — G. LUDWIG, Comm. Math. Phys. **4**, 331 [1967].