Adiabatic *vs* Bloch Approximation in Lattice Scattering of Electrons*

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The time dependence of an electron-phonon system described by means of Born-Oppenheimer states is shown to be the same to first order in the coupling as the usual Bloch theory.

INTRODUCTION

AN important problem in transport theory is the separation of the scattered part from the other deformations of the conduction electron state due to lattice vibrations. In the treatment due to Bloch the scattering is calculated in first-order time-dependent perturbation theory. The unperturbed states are products of perfect-lattice electron states and lattice oscillator states. The perturbation is the change in potential produced by the lattice deformation. No other effects of the perturbation are considered.

It has been suggested[1] that it would be better to start with adiabatic states of the Born-Oppenheimer (B-O) type since these already include a correlation of the electron and lattice motions. Ziman and Haug have shown independently by direct calculation that the matrix elements of the nonadiabatic part (H^{NA}) of the Hamiltonian are closely related to those of the Bloch theory. Thus the effect of H^{NA}, treated as a perturbation, is not smaller than in the Bloch theory so that it is not obvious that the B-O states are a better starting approximation. It is shown in this note that the time dependence of states calculated by the B-O and Bloch methods is the same to *first order* in the electron-lattice coupling. This result, of course, has no bearing on the utility of the adiabatic approximation in an intermediate- or strong-coupling calculation.

CONSTRUCTION OF THE B-O FUNCTIONS

The B-O functions have some peculiar properties in perturbation calculations because of the definition of H^{NA}. We briefly review them here for the electron-lattice problem. Complex normal coordinates Q_q specify the displacement of the modes $q=(\mathbf{q},\sigma)$. The Hamiltonian is

$$\begin{aligned}H&=H_E+H_L+H_I\\&=H_E+\tfrac{1}{2}\textstyle\sum_q(P_q^\dagger P_q+\omega_q^2 Q_q^\dagger Q_q)\\&\qquad+N^{-\frac{1}{2}}\textstyle\sum_q V_q(\mathbf{r})e^{i\mathbf{q}\cdot\mathbf{r}}Q_q.\end{aligned}\tag{1}$$

It is split up in two different ways:

$$\begin{aligned}&H_0+H_1=(H_E+H_L)+H_I, &&\text{Bloch method;}\\&H_0'+H_1'=(H_E+H_L{}^A+H_I)+H^{NA}, &&\text{B-O method;}\end{aligned}\tag{2}$$

where $H_L{}^A$ and H^{NA} are defined for the product functions $\Phi=\phi(\mathbf{r};Q)\chi(Q)$ by

$$H_L{}^A\phi\chi=\phi H_L\chi,\tag{3a}$$

$$\begin{aligned}H^{NA}\phi\chi&=(H-H_L{}^A)\phi\chi\\&=\tfrac{1}{2}\textstyle\sum_q\{(P_q^\dagger\phi)(P_q\chi)+(P_q\phi)(P_q^\dagger\chi)\\&\qquad+(P_q^\dagger P_q\phi)\chi\}.\end{aligned}\tag{3b}$$

Here ϕ and χ are the normalized eigenfunctions satisfying

$$(H_E+H_I)\phi_l(\mathbf{r};Q)=\mathcal{E}_l(Q)\phi_l(\mathbf{r};Q);\tag{4a}$$

$$[H_L+\mathcal{E}_l(Q)]\chi_{l\nu}(Q)=E_{l\nu}\chi_{l\nu}(Q).\tag{4b}$$

The customary running-wave operators, $a=(Q+iP^\dagger)/\sqrt{2}$, etc., are not used because Q and P are treated differently in the adiabatic approximation.

The $\Phi_{l\nu}=\phi_l\chi_{l\nu}$ form a complete orthonormal set, and by expansion the linear operations $H_L{}^A$ (and H^{NA}) can be defined for the general state $\Psi=\sum c_{l\nu}\Phi_{l\nu}$:

$$H_L{}^A\Psi\equiv\textstyle\sum c_{l\nu}H_L{}^A\Phi_{l\nu}.\tag{5}$$

This operation is Hermitian because the $E_{l\nu}$ are real. $H^{NA}=H_L-H_L{}^A$ is also Hermitian. It is thus possible to do the usual perturbation calculations with H_0' and H_1' but the calculation is constrained to be done explicitly in terms of the $\Phi_{l\nu}$ (B-O representation). The latter restriction mars the formal similarity to perturbation theory since the functions $\Phi_{l\nu}$ are not known exactly. Suppose v, η are approximations to ϕ, χ, respectively:

$$v(\mathbf{r};Q)=\textstyle\sum_l a_l(Q)\phi_l(\mathbf{r};Q),$$

$$a_l(Q)\eta(Q)=\textstyle\sum_\nu a_{l\nu}\chi_{l\nu}(Q);$$

so that

$$v\eta=\textstyle\sum_{l\nu}a_{l\nu}\Phi_{l\nu}.$$

In $H_L{}^A(v\eta)\equiv vH_L\eta$ the lattice coordinates in $a_l(Q)$ are not differentiated, but they clearly are differentiated in $\sum a_{l\nu}H_L{}^A\Phi_{l\nu}$. The separation $H_L{}^A+H^{NA}$ can be defined only to the accuracy of the approximate B-O functions.

The electronic functions will now be calculated to first order in terms of the Bloch functions:

$$\Psi_{\mathbf{k}n}=u_{\mathbf{k}}(\mathbf{r})\prod_q u_{n_q}(Q_q);$$

$$H_0\Psi_{\mathbf{k}n}=E_{\mathbf{k}n}{}^{(0)}\Psi_{\mathbf{k}n};$$

$$E_{\mathbf{k}n}{}^{(0)}=\epsilon(\mathbf{k})+E_n=\epsilon(\mathbf{k})+\textstyle\sum_q(n_q+\frac{1}{2})\hbar\omega_q.$$

To this order $\mathbf{k}$, n will be good quantum numbers so

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[1] J. R. Ziman, Proc. Cambridge Phil. Soc. **51**, 707 (1955); H. Stumpf, Z. Naturforsch. **11a**, 259 (1956); A. Haug, Z. Physik **146**, 75 (1956).

that the transformation from the Bloch to B-O representation is

$$\Phi_{\mathbf{k}n}=\mathcal{U}\Psi_{\mathbf{k}n}. \tag{6}$$

In a familiar manner the electronic part is first found in (4a) to some order in λ, where H_I is replaced by λH_I, and $\mathcal{E}_{\mathbf{k}}(Q)=\mathcal{E}_{\mathbf{k}}^{(0)}+\lambda\mathcal{E}_{\mathbf{k}}^{(1)}+\cdots$ is put in (4b) $[\mathcal{E}_{\mathbf{k}}^{(0)}=\epsilon(\mathbf{k})]$. Since H_I is linear in Q_q,

$$\mathcal{E}_{\mathbf{k}}^{(1)}(Q)=\sum_q Q_q\left.\frac{\partial\mathcal{E}_{\mathbf{k}}}{\partial Q_q}\right|_{Q_q=0}, \tag{7}$$

and similarly for $\mathcal{E}_{\mathbf{k}}^{(2)}$, etc. For the electronic part, the lowest order terms are[2]

$$\phi_{\mathbf{k}}(\mathbf{r};Q)=u_{\mathbf{k}}(\mathbf{r})+\lambda\sum_{\mathbf{k}'\neq\mathbf{k}}\frac{H_{I\mathbf{k}'\mathbf{k}}}{\epsilon(\mathbf{k}')-\epsilon(\mathbf{k})}u_{\mathbf{k}'}+\cdots; \tag{8}$$

$$H_{I\mathbf{k}'\mathbf{k}}=(u_{\mathbf{k}'},H_I u_{\mathbf{k}})=N^{-\frac{1}{2}}U_q(\mathbf{k}',\mathbf{k})Q_q,\quad \mathbf{q}=\mathbf{k}'-\mathbf{k};$$

$$U_q(\mathbf{k}',\mathbf{k})=(u_{\mathbf{k}'},U_q(\mathbf{r})u_{\mathbf{k}})\propto\delta_{\mathbf{k}',\mathbf{k}+\mathbf{q}};$$

$$\mathcal{E}_{\mathbf{k}}(Q)=\epsilon(\mathbf{k})+\lambda H_{I\mathbf{k}\mathbf{k}}+\frac{\lambda^2}{N}\sum_q\frac{|U_q(\mathbf{k}+\mathbf{q},\mathbf{k})|^2}{\epsilon(\mathbf{k}+\mathbf{q})-\epsilon(\mathbf{k})}Q_q^{\dagger}Q_q+\cdots. \tag{9}$$

Since $H_{I\mathbf{k}\mathbf{k}}\propto N^{-\frac{1}{2}}Q_0$, the term linear in λ is negligible for large N. The N^{-1} before the quadratic term is canceled by the terms $\propto N$ in the summation. There is *no first-order* change in the lattice motion:

$$\chi_{\mathbf{k}n}=\chi_{\mathbf{k}n}^{(0)}+\lambda^2\chi_{\mathbf{k}n}^{(2)}+\cdots=\prod_q u_{n_q'}(Q_q)+\cdots; \tag{10}$$

where $u_{n_q'}$ is u_{n_q} with ω_q replaced by

$$\omega_q'=\omega_q+\frac{\lambda^2}{\hbar N}\frac{|U_q(\mathbf{k}+\mathbf{q},\mathbf{k})|^2}{\epsilon(\mathbf{k}+\mathbf{q})-\epsilon(\mathbf{k})}.$$

The change in u_{n_q} is of order N^{-1}:

$$\delta u_{n_q}=\tfrac{1}{4}(\delta\omega_q/\omega_q)\{-(n_q+1)^{\frac{1}{2}}(n_q+2)^{\frac{1}{2}}u_{n_q+2}+n_q^{\frac{1}{2}}(n_q+1)^{\frac{1}{2}}u_{n_q-2}\},$$

but the change in χ is of order unity or more precisely of order

$$\lambda^2\chi^{(0)}\langle|U_q|^2/\hbar\omega_q[\epsilon(\mathbf{k}+\mathbf{q})-\epsilon(\mathbf{k})]\rangle_{\mathrm{Av}}.$$

Writing the transformation operation in (6) as $\mathcal{U}=\mathcal{U}^{(0)}+\lambda\mathcal{U}^{(1)}+\cdots$, then, since in first order only $\phi_{\mathbf{k}}$ changes, the matrix $\mathcal{U}_{\mathbf{k}'n',\mathbf{k}n}=(\Psi_{\mathbf{k}'n'},\Phi_{\mathbf{k}n})$ is, to first order in λ,

$$\mathcal{U}_{\mathbf{k}'n',\mathbf{k}n}^{(0)}=\delta_{\mathbf{k}'n',\mathbf{k}n},$$

and for $\mathbf{k}'n'\neq\mathbf{k}n$

$$\mathcal{U}_{\mathbf{k}'n',\mathbf{k}n}^{(1)}=[\epsilon(\mathbf{k}')-\epsilon(\mathbf{k})]^{-1}H_{I\mathbf{k}'n',\mathbf{k}n}, \tag{11}$$

where only n_q' differs from n_q so that

$$H_{I\mathbf{k}'n',\mathbf{k}n}=N^{-\frac{1}{2}}U_q(\mathbf{k}',\mathbf{k})Q_q(n_q',n_q).$$

The diagonal elements of $\mathcal{U}^{(1)}$ are zero. It is convenient to write $\mathcal{U}^{(1)}$ also as a matrix in the electronic states only. Then

$$\mathcal{U}_{\mathbf{k}',\mathbf{k}}^{(1)}(Q)=N^{-\frac{1}{2}}U_q(\mathbf{k}',\mathbf{k})[\epsilon(\mathbf{k}')-\epsilon(\mathbf{k})]^{-1}Q_q, \tag{12}$$

$$\Phi_{\mathbf{k}n}=\{u_{\mathbf{k}}+\lambda\textstyle\sum_{\mathbf{k}'}\mathcal{U}_{\mathbf{k}'\mathbf{k}}^{(1)}(Q)u_{\mathbf{k}'}+O(\lambda^2)\}\times\{\chi_{\mathbf{k}n}^{(0)}+O(\lambda^2)\}. \tag{13}$$

H^{NH} will operate on the Q_q in $\mathcal{U}^{(1)}(Q)$ and will thereby have a comparable effect to H_I.

TIME DEPENDENCE

In terms of the separation $H=H_0'+H_1'$, the time dependence of the Schrödinger state vector is

$$\Psi(t)=\exp(-iH_0't/\hbar)\times\exp_+\left(-i\int_0^t H^{NA}(\tau)d\tau/\hbar\right)\Psi(0), \tag{14}$$

where the operations are all defined in the B-O representation and

$$H^{NA}(\tau)=\exp(iH_0'\tau/\hbar)H^{NA}\exp(-iH_0'\tau/\hbar).$$

The ordered exponential[3] $\exp_+(\cdots)$ is not used seriously since we are only interested in first order terms in λ. Because of the proviso in the definition of H^{NA}, it will be better to work explicitly in the B-O representation. The column vector for Ψ will be denoted by $\mathcal{C}$ here and by $\mathcal{C}'$ in the Bloch representation. According to (6), $\Phi_{\mathbf{k}n}=\sum\mathcal{U}_{\mathbf{k}'n',\mathbf{k}n}\Psi_{\mathbf{k}'n'}$ so that $\mathcal{C}'=\mathcal{U}\mathcal{C}$ where $\mathcal{U}$ is the matrix (11). Then

$$\mathcal{C}'(t)=\mathcal{U}\exp(-iH_0't/\hbar)\mathcal{U}^{-1}\mathcal{U}\exp_+(\cdots)\mathcal{C}(0). \tag{15}$$

Again $\mathcal{C}(0)$ is kept on the right side because H^{NA} is defined in that representation. To first order in λ,

$$\exp_+\left(-i\int_0^t H^{NA}(\tau)d\tau/\hbar\right)=1-i\int_0^t H^{NA}(\tau)d\tau/\hbar,$$

since H^{NA} operating on the $\lambda\mathcal{U}^{(1)}$ term in (13) is of order λ. The identity in the above gives in (15) the term,

$$\mathcal{U}\exp(-iH_0't/\hbar)\mathcal{U}^{-1}\mathcal{C}'(0),$$

which is just the evolution of unperturbed (by H^{NA}) B-O states as seen in the Bloch picture.

Upon using the B-O matrix,

$$\exp(-iH_0't/\hbar)_{\mathbf{k}'n',\mathbf{k}n}=\delta_{\mathbf{k}'n',\mathbf{k}n}\exp(-iE_{\mathbf{k}'n'}^{(0)}t/\hbar),$$

[2] The possibility of a reciprocal lattice vector here is understood.

[3] R. P. Feynman, Phys. Rev. **84**, 108 (1951).

this part of (15) is

$$\mathcal{C}_{\mathbf{k}'n'}'(t)=\exp(-iE_{\mathbf{k}'n'}^{(0)}t/\hbar)\times\Big\{\mathcal{C}_{\mathbf{k}'n'}'(0)+\lambda\sum_{\mathbf{k}n\neq\mathbf{k}'n'}H_{I\mathbf{k}'n',\mathbf{k}n}\times\left(\frac{\exp[i(E_{\mathbf{k}'n'}^{(0)}-E_{\mathbf{k}n}^{(0)})t/\hbar]-1}{\epsilon(\mathbf{k}')-\epsilon(\mathbf{k})}\right)\times\mathcal{C}_{\mathbf{k}n}'(0)\Big\}+O(\lambda^2). \quad (16)$$

This resembles closely the form of the Bloch theory but for the appearance of the electronic energy in the denominators of the transition terms while the total energy appears in the numerator. The difference in the two is the energy of a phonon, so that in the limit of very low-frequency phonons or static lattice deformations the scattering is described as the "spreading" of Bloch-state wave packets constructed out of *stationary* B-O states.

The H^{NA} matrix elements in (15) are

$$\left(\Phi_{\mathbf{k}'n'},-i\int_0^t\exp(iH_0'\tau/\hbar)H^{NA}\times\exp(-iH_0'\tau/\hbar)d\tau/\hbar\Phi_{\mathbf{k}n}\right)=-\lambda\left(\frac{\exp[i(E_{\mathbf{k}'n'}^{(0)}-E_{\mathbf{k}n}^{(0)})t/\hbar]-1}{E_{\mathbf{k}'n'}^{(0)}-E_{\mathbf{k}n}^{(0)}}\right)\times(\Phi_{\mathbf{k}'n'},H^{NA}\mathcal{U}^{(1)}(Q)\Psi_{\mathbf{k}n}). \quad (17)$$

Now Q appears linearly in $\mathcal{U}^{(1)}(Q)$ according to (12), and by (13) and (3b) the quantity $H^{NA}\mathcal{U}^{(1)}(Q)\Psi_{\mathbf{k}n}$ contains terms like $[P_q\mathcal{U}^{(1)}(Q)][P_q{}^\dagger\Psi_{\mathbf{k}n}]$, $[P_q{}^\dagger\mathcal{U}^{(1)}(Q)]\times[P_q\Psi_{\mathbf{k}n}]$, and $[P_q{}^\dagger P_q\mathcal{U}^{(1)}(Q)]\Psi_{\mathbf{k}n}$, the last term vanishing. Now $P_q\mathcal{U}^{(1)}(Q)=-i\hbar(\partial/\partial Q_q)\mathcal{U}^{(1)}(Q)$ removes Q_q which is replaced by $-i\hbar P_q{}^\dagger$ operating on $\Psi_{\mathbf{k}n}$. But $-i\hbar P_q{}^\dagger=[H_L,Q_q]$ so that

$$H^{NA}\mathcal{U}^{(1)}(Q)\Psi_{\mathbf{k}n}=\mathcal{U}^{(1)}([H_L,Q])\Psi_{\mathbf{k}n}.$$

Neglecting all other terms of order λ in (15) which multiply H^{NA} gives as the additional first-order contribution to (16):

$$-\lambda\exp(-iE_{\mathbf{k}'n'}^{(0)}t/\hbar)\sum_{\mathbf{k}n}\mathcal{U}^{(1)}([H_L,Q])_{\mathbf{k}'n',\mathbf{k}n}\times\left(\frac{\exp[i(E_{\mathbf{k}'n'}^{(0)}-E_{\mathbf{k}n}^{(0)})t/\hbar]-1}{E_{\mathbf{k}'n'}^{(0)}-E_{\mathbf{k}n}{}'^{(0)}}\right)\mathcal{C}_{\mathbf{k}n}'(0). \quad (18)$$

Now using (11), we have

$$\mathcal{U}^{(1)}([H_L,Q])_{\mathbf{k}'n',\mathbf{k}n}=(E_{n'}-E_n)\mathcal{U}_{\mathbf{k}'n',\mathbf{k}n}^{(1)}=\frac{(E_{n'}-E_n)}{\epsilon(\mathbf{k}')-\epsilon(\mathbf{k})}H_{I\mathbf{k}'n',\mathbf{k}n}. \quad (19)$$

This matrix element, which is just the matrix element of H^{NA} in (17) in the B-O representation, was given by Ziman and Haug.[1] The "nonadiabatic" terms (18) can be combined with (16) if the resonance denominator is put in the latter by writing

$$[\epsilon(\mathbf{k}')-\epsilon(\mathbf{k})]^{-1}=\{(E_{\mathbf{k}'n'}^{(0)}-E_{\mathbf{k}n}^{(0)})/[\epsilon(\mathbf{k}')-\epsilon(\mathbf{k})]\}\times(E_{\mathbf{k}'n'}^{(0)}-E_{\mathbf{k}n}^{(0)})^{-1}.$$

Then (16) and (18) combine through

$$\frac{E_{\mathbf{k}'n'}^{(0)}-E_{\mathbf{k}n}^{(0)}}{\epsilon(\mathbf{k}')-\epsilon(\mathbf{k})}-\frac{E_{n'}-E_n}{\epsilon(\mathbf{k}')-\epsilon(\mathbf{k})}=1,$$

to give the first-order term of the Bloch theory.

DISCUSSION

It is not surprising that when *all* contributions of order λ are accounted for, the result is the same for different separations into time-independent ($\Psi_{\mathbf{k}n}$ *vs* $\Phi_{\mathbf{k}n}$) and time-dependent (H_I *vs* H^{NA}) parts. This should be true for any order in a strict reduction to powers of λ. There seems to be no advantage, then, to using B-O initial states in first order nor any significance attached (in disagreement with Ziman) to the mixing of states of the *same* electron energy through the denominator in (19). In fact, in the construction of the B-O states the degeneracy in (8) was ignored and it is the energy denominators there that are responsible for (19). The reduction to the Bloch theory shows that there is a cancellation of these terms and that the mixing which does occur is between states $E_{\mathbf{k}'n'}^{(0)}=E_{\mathbf{k}n}^{(0)}$.

Transport phenomena which depend on the lowest order of the electron-phonon coupling are appropriately described by the Bloch theory. This is in agreement with the general arguments of Van Hove[4] in his development of the quantum-mechanical transport equation where the lowest order interaction effects are shown to be dissipative.[5]

[4] L. Van Hove, Physica **21**, 517 (1955).

[5] The author wishes to thank Professor Van Hove for pointing this out to him.