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The Interaction of Electrons in Metals and Insulators

C. W. UFFORD*
Palmer Physical Laboratory, Princeton University, Princeton, New Jersey

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The electrostatic energy of electrons in a lattice has been calculated by the Rayleigh-Schrödinger perturbation method. This method gives a value which becomes logarithmically infinite for a metal. For an insulator, however, the gap in energy above the first occupied zone leads to a finite result. Numerical values have been found for the three cases in which the gap is one-half the width of the first zone, equal in width, and twice as wide.

1. INTRODUCTION

THE customary approximation for the solution of problems of atomic or crystal physics is the Hartree-Fock approximation. The question of deviations from this approximation and of an improvement of the underlying picture deserves therefore considerable attention.

We shall be concerned with the case of doubly occupied orbits, i.e., with such states in which each orbit is either empty, or occupied by two electrons with opposite spins. It is well known that in this case, for the calculation of the electrostatic and kinetic energy, one can use a wave function of the form

$$\Psi_0=\frac{1}{n!}\begin{vmatrix}\psi_1(x_1)\cdots\psi_1(x_n)\\ \psi_2(x_1)\cdots\psi_2(x_n)\\ \cdot \qquad \cdot\\ \cdot \qquad \cdot\\ \cdot \qquad \cdot\\ \psi_n(x_1)\cdots\psi_n(x_n)\end{vmatrix}\begin{vmatrix}\psi_1(y_1)\cdots\psi_1(y_n)\\ \psi_2(y_1)\cdots\psi_2(y_n)\\ \cdot \qquad \cdot\\ \cdot \qquad \cdot\\ \cdot \qquad \cdot\\ \psi_n(y_1)\cdots\psi_n(y_n)\end{vmatrix}. \qquad (1)$$

The number of electrons is $2n$, the symbols $x_1, \cdots, x_n, y_1, y_n$ stand for three-space coordinates each. The x denote coordinates of electrons with one-spin orientation, the y coordinates of electrons with opposite spin orientation. The $\psi_1, \cdots, \psi_n$ are orthogonal and normalized wave functions, representing the n occupied orbits. The wave function (1) represents, of course, a singlet state of the system.

Two methods have been tried so far to obtain an improvement of the wave function (1). The first one is essentially based on the variational idea: The sum of kinetic and potential energies of more general wave functions than given by (1) is calculated and the functions and parameters which occur in this wave function are determined by the requirement that the total energy be a minimum. The difficulty encountered is that it is, in the case of many electrons, not easy to find a wave function for which the total energy can be calculated. For a small number of electrons, on the other hand, the variational method is relatively easily applied and converges in many cases rapidly.[1] Even in the case of many electrons, in particular crystals, some success has been achieved by this method.[2]

The second method which will be tested in the present paper is the Rayleigh-Schrödinger perturbation method. The application of this method encounters relatively small difficulties in the case of only doubly occupied orbits, because the original state is not degenerate and the successive approximations are easily obtained in the form of infinite series.[3] It is generally assumed that the successive approximations converge in the case of a small number of particles, that is when n is small. In the case of n large, with which we will be concerned, the question of convergence is more complicated and we first turn to a discussion of this question.

If the state considered is nondegenerate, the first approximation for the energy in the Rayleigh-Schrödinger scheme is given by the expression

$$E^{(1)}=E_0=\int\Psi_0{}^*H\Psi_0, \qquad (2)$$

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* On sabbatical leave from Allegheny College, Meadville, Pennsylvania.

[1] Cf. the well-known papers of Hylleraas and James and Coolidge.

[2] E. Wigner, Phys. Rev. **46**, 1002 (1934); Trans. Faraday Soc. **34**, 678 (1938).

[3] L. Brillouin, J. de phys. et rad. [7] **3**, 565 (1932); S. Flugge, Zeits. f. Physik **96**, 459 (1935); S. Watanabe, Zeits. f. Physik **113**, 482 (1939).

The conclusions reached in the present paper are, however, in many respects different from those of these authors.

where H is the Hamiltonian. This is the energy in the Hartree-Fock approximation. In the second approximation, the wave function is given by

$$\Psi_0{}^{(2)}=\Psi_0+\sum_l a_l\Psi_l, \tag{3}$$

$$a_l=\int \Psi_l{}^*H\Psi_0/E_0-E_l. \tag{3a}$$

Here Ψ_l are wave functions of the form (1) with the difference, however, that the orbits occurring in the determinants are not the occupied orbits of Ψ_0 but at least partly other members of a complete orthonormal set which contains $\psi_1, \cdots, \psi_n$. In the "excited states" Ψ_l, the two determinants are in general different because in these states the orbits are not all doubly occupied. $E_l=\int\Psi_l{}^*H\Psi_l$ is the first approximation to the energy of the excited state l. The energy of the lowest state becomes in the second approximation

$$\begin{aligned} E^{(2)}&=E^1+\sum_l \frac{|\int\Psi_l{}^*H\Psi_0|^2}{E_0-E_l} \\ &=E_1+\sum_l (E_0-E_l)|a_l|^2. \end{aligned} \tag{4}$$

The summation over l must be extended in (3) and (4) over all possible excited states, i.e., over all wave functions in which the two determinants contain any n orbits ψ.

If the Hamiltonian contains, in addition to the kinetic energy, only terms each of which involves the coordinates of not more than two particles, i.e., two-particle interactions alone, a considerable simplification can be effected. In this case, a_l vanishes if Ψ_l contains more than two orbits not contained in Ψ_0. This can be seen directly upon writing down the integral occurring in (3a). As a consequence hereof, the wave function $\Psi_0{}^{(2)}$ contains only those states Ψ_l in which not more than two particles are "excited" to states different from $\psi_1, \cdots, \psi_n$. (We shall see later that only such states occur in which two excited electrons are present in (3).) This means, physically, that a measurement of the number of electrons present in the states $\psi_1, \cdots, \psi_n$ gives at least the value $2n-2$, and possibly the value $2n$. For n large this is, of course, an unreasonable result as one will expect that the number of excited electrons is roughly proportional to n. This is also obtained when the variational method is used. In addition to this difficulty, in all cases in which calculations have been carried out so far, the sum of the squares of the a_l increases, with increasing n, beyond all bounds so that the wave function (3) cannot be normalized. Not only does (3) fail to contain all excited states which it should, but it contains more of some than it should. It is evident, therefore, that in the case of n large, (3) is not an approximate wave function in the usual sense, and it could be used only if the statistical interpretation is used in a modified form.[4] The reason for this difficulty is that Ψ_0 is not a good first approximation. Doubtless, for the real stationary state, the probability is vanishingly small that all electrons shall be in the unexcited states $\psi_1, \cdots, \psi_n$. Hence the coefficient of Ψ_0 is vanishingly small in the correct wave function while it is 1 in (3).

It will be seen that in spite of this, under certain conditions, the expression (4) for the energy gives a reasonable result even in the case of n very large. This hardly can be interpreted as the expectation value of the energy for the wave function (3)—because this wave function cannot be normalized and would give an entirely different result if it could be. It can be considered, however, as the second-order term in a power series expansion of the total energy, in terms of the fictitious parameter with which the perturbation energy appears to be multiplied in the Rayleigh-Schrödinger scheme.

It remains, of course, questionable whether this power series for the total energy converges for as large a value of the parameter as is assumed in the actual problem. It is quite conceivable that the radius of convergence of the Rayleigh-Schrödinger series decreases with increasing n so that, for n large, it is smaller than the value which this parameter actually has. It is also possible that the number of terms needed in order to obtain a reasonable approximation increases with increasing n, while, in practice, one can proceed only to the second term.

In order to test this method it has been applied to two problems: the electron interaction in

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[4] This has been essentially proposed by Watanabe, reference 2.

metals and the electron interaction in insulators. In the first case, it was assumed that the wave functions occurring in (1) are plane waves, i.e., that there is no lattice field present. Although this corresponds to a fictitious uniform distribution of the positive charges, it is in reality for many cases not a bad approximation to the true Hartree-Fock wave function. In this case, the series (4) gives a correction which increases, with increasing n, more rapidly than n itself. Hence, the energy correction per particle, obtained from (4), increases beyond all bounds, with increasing n—an evidently incorrect conclusion. We believe that this result is independent of the approximations employed. In this case, the Rayleigh-Schrödinger theory cannot be applied.

In the case of an insulator, the lowest E_l is at a finite distance from E_0—the distance of the gap between the first two Brillouin zones. In this case E_0-E_l cannot become arbitrarily small. For the wave functions $\psi_1, \psi_2, \cdots$ we shall use in this case the expressions given by Peierls[5] for the case of weak lattice fields. Although in this way only a few wave functions are very different from plane waves, those matrix elements which were very large for free electrons are materially reduced. The whole sum (4) becomes proportional to n. This gives a constant energy correction per particle which is, furthermore, of the right order of magnitude. This proves, of course, only that our result is reasonable, not that it is correct. In fact, it cannot be correct if the condition for Peierls' approximation is satisfied, i.e., if the lattice potential is very nearly constant. For a constant potential, we have again the case of free electrons in which (4) breaks down. In fact, we obtain an energy correction per particle which increases beyond limits if the lattice field becomes vanishingly weak, a result which cannot be correct. Our result can be correct, however, for moderately strong lattice fields.

In justice to the Rayleigh-Schrödinger method, it should be pointed out that (4) always gives finite results in case of short range forces as they occur in nuclei.[6] Whether this finite result is correct remains, in my opinion, an open question.

2. The Electron Interaction in Metals

First the matrix elements a_l of (3a) must be calculated for $H=e^2/r_{ij}$ to find the electrostatic energy of interaction of the electrons. Substituting the wave functions (1) in (3a) gives for the integral

$$\int \Psi_l^*(e^2/r_{ij})\Psi_0=\frac{e^2}{V^{2n}(n!)^2}\int \begin{vmatrix} \psi_1^*(x_1)\cdots\psi_1^*(x_n) \\ \cdot \qquad\qquad \cdot \\ \cdot \qquad\qquad \cdot \\ \cdot \qquad\qquad \cdot \\ \psi_n^*(x_1)\cdots\psi_n^*(x_n) \end{vmatrix} \begin{vmatrix} \psi_1^*(y_1)\cdots\psi_1^*(y_n) \\ \cdot \qquad\qquad \cdot \\ \cdot \qquad\qquad \cdot \\ \cdot \qquad\qquad \cdot \\ \psi_n^*(y_1)\cdots\psi_n^*(y_n) \end{vmatrix}$$

$$\times\frac{1}{r_{ij}} \begin{vmatrix} \psi_1(x_1)\cdots\psi_1(x_n) \\ \cdot \qquad\qquad \cdot \\ \cdot \qquad\qquad \cdot \\ \cdot \qquad\qquad \cdot \\ \psi_n(x_1)\cdots\psi_n(x_n) \end{vmatrix} \begin{vmatrix} \psi_1(y_1)\cdots\psi_1(y_n) \\ \cdot \qquad\qquad \cdot \\ \cdot \qquad\qquad \cdot \\ \cdot \qquad\qquad \cdot \\ \psi_n(y_1)\cdots\psi_n(y_n) \end{vmatrix} dxdy, \qquad (5)$$

where $dx=dx_1\cdots dx_n$ and $dy=dy_1\cdots dy_n$. For plane waves

$$\psi_k(x_i)=\exp\left[i\mathbf{k}\cdot\mathbf{x}_i\right] \quad \text{and} \quad E_k=\hbar^2k^2/2m. \qquad (6)$$

The components of $\mathbf{k}$ have the form $2\pi n_x/L$, $2\pi n_y/L$, and $2\pi n_z/L$ where n_x, n_y and n_z are integers' and L is the length of an edge of the crystal, $L^3=V$. The functions ψ_k are normalized and orthogona so that

$$(1/V)\int \psi_k^*(x_i)\psi_{k'}(x_i)dx_i=\delta_{kk'}. \qquad (7)$$

As will be shown presently, the matrix elements for which only one electron is excited vanish. Therefore only those with two electrons excited will be considered. There will be two types of matrix

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[5] R. Peierls, Ann. d. Physik **4**, 121 (1930).

[6] S. Watanabe, S. Flugge, reference 3.

elements: those for which two electrons with parallel spin are excited, and those for which two electrons with antiparallel spin are excited. As the greater contribution to (4) arises from the second type, it will be sufficient to consider it alone.

Let $\mathbf{k}$ and $\mathbf{k}'$ be two wave vectors in the reciprocal lattice which represent unexcited or occupied states, and $\mathbf{l}$ and $\mathbf{l}'$ wave vectors representing excited states. In the sum over $\mathbf{kk'll'}$ to obtain the energy of all the electrons in (4), $\mathbf{k}$ and $\mathbf{k}'$ must be vectors to all points inside the sphere of momentum space whose radius represents the highest occupied state, and $\mathbf{l}$ and $\mathbf{l}'$ must be over points outside this sphere. The matrix elements (5) may then be written

$$V_{\mathrm{kk'll'}}=\frac{e^2}{V^{2n}}\int\begin{vmatrix}\psi_1(x_1)\cdots\psi_1(x_n)\\ \cdot \qquad \cdot\\ \cdot \qquad \cdot\\ \cdot \qquad \cdot\\ \psi_n(x_1)\cdots\psi_n(x_n)\end{vmatrix}\begin{vmatrix}\psi_1(y_1)\cdots\psi_1(y_n)\\ \cdot \qquad \cdot\\ \cdot \qquad \cdot\\ \cdot \qquad \cdot\\ \psi_n(y_1)\cdots\psi_n(y_n)\end{vmatrix}\frac{1}{|x_i-y_{i'}|}\psi_1{}^*(x_1)\cdots\psi_n{}^*(x_n)\psi_1{}^*(y_1)\cdots\psi_n{}^*(y_n)dxdy, \tag{8}$$

since the same terms are obtained from the diagonal of the complex conjugate matrices as are obtained from each of the other terms. As there are $n!$ terms in each matrix, the $(n!)^2$ cancels out. Again

$$V_{\mathrm{kk'll'}}=\frac{e^2}{V^2}\int\psi_k(x_k)\psi_{k'}(y_{k'})\frac{1}{|x_k-y_{k'}|}\psi_l{}^*(x_k)\psi_{l'}{}^*(y_{k'})dx_kdy_{k'}, \tag{9}$$

as the integration over all coordinates except x_k and $y_{k'}$ gives unity because of the normalization of the $\psi_k(x_i)$s. Here k and k' represent electrons with opposite spins. The parts of the matrix elements with parallel spin, where both electrons have the coordinates x or both y, are neglected. Because of exchange, these parts contain the difference of two terms which are nearly equal at those points where these parts have their largest value. Thus these parts are small compared to the one calculated in (9).

Now if plane waves are introduced and a transformation

$$\mathbf{x}_k-\mathbf{y}_{k'}=2\boldsymbol{\varrho},\quad \mathbf{x}_k+\mathbf{y}_{k'}=2\boldsymbol{\sigma} \tag{10}$$

of Jacobian 8, then

$$V_{\mathrm{kk'll'}}=\frac{4e^2}{V^2}\int\exp\left[i(\mathbf{k}-\mathbf{l}+\mathbf{k}'-\mathbf{l}')\cdot\boldsymbol{\sigma}+(\mathbf{k}-\mathbf{l}-\mathbf{k}'+\mathbf{l}')\cdot\boldsymbol{\varrho}\right]\frac{d\boldsymbol{\sigma}d\boldsymbol{\varrho}}{|\boldsymbol{\varrho}|} \tag{11}$$

$$=\frac{4e^2}{V}\int\exp\left[i(\mathbf{k}-\mathbf{l}+\mathbf{k}'+\mathbf{l}')\cdot\boldsymbol{\varrho}\right]\frac{d\boldsymbol{\varrho}}{|\boldsymbol{\varrho}|}\delta(\mathbf{k}+\mathbf{k}'-\mathbf{l}-\mathbf{l}'), \tag{12}$$

because of the orthonormality of the σ waves.

If only one electron is excited, then $\mathbf{l}'=\mathbf{k}'$ and the factor $\delta(\mathbf{k}-\mathbf{l})$ gives a factor zero, since if one electron is excited $\mathbf{k}\neq\mathbf{l}$. Thus all matrix elements with a single electron excited are zero.

The integral over $\boldsymbol{\varrho}$ gives

$$\int\exp\left[i\boldsymbol{\alpha}\cdot\boldsymbol{\varrho}\right]d\boldsymbol{\varrho}/|\boldsymbol{\varrho}|=-4\pi/|\boldsymbol{\alpha}|^2, \tag{13}$$

so that

$$V_{\mathrm{kk'll'}}=-\frac{16\pi e^2}{V}\frac{\delta(\mathbf{k}+\mathbf{k}'-\mathbf{l}-\mathbf{l}')}{|\mathbf{k}-\mathbf{l}-\mathbf{k}'+\mathbf{l}'|^2}=-\frac{4\pi e^2}{V}\frac{1}{|\mathbf{l}-\mathbf{k}|^2}\delta(\mathbf{k}+\mathbf{k}'-\mathbf{l}-\mathbf{l}'). \tag{14}$$

The energy may now be calculated by substituting (6) and (14) in (4). The second-order term is

$$E=\sum\nolimits_{\mathrm{kk'll'}}\frac{|V_{\mathrm{kk'll'}}|^2}{E_k+E_{k'}-E_l-E_{l'}}=-\frac{16\pi^2e^4m}{V^2\hbar^2}\sum\nolimits_{\mathrm{kk'll'}}\frac{\delta(\mathbf{k}+\mathbf{k}'-\mathbf{l}-\mathbf{l}')}{|\mathbf{l}-\mathbf{k}|^4(\mathbf{l}-\mathbf{k})\cdot(\mathbf{l}-\mathbf{k}')}. \tag{15}$$

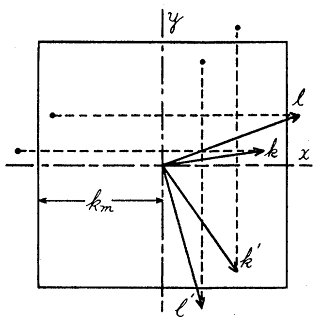

FIG. 1. Wave vectors **k** and **k'** in the xy plane for the normal states inside the first zone, and **l** and **l'** for the excited states outside the zone. It will be seen that these vectors satisfy the condition that $\mathbf{l}-\mathbf{k}=\mathbf{k}'-\mathbf{l}'$. k_m is the vector to the boundary of the first zone.

This sum can be evaluated as a special case of the sum considered later for insulators. It is found to approach infinity logarithmically.[7] This is due to the difference of the wave vectors of the normal and excited states in the denominator of (15). This denominator approaches zero as the wave vectors approach each other at the boundary of the occupied states. In insulators, on the other hand, there is a gap in energy at this boundary with the first energy band completely filled. The gap will introduce a term in the denominator which will prevent the energy from becoming infinite. This question of insulators will be considered.

In (15), the energy of the free electron, $E_k=\hbar^2k^2/2m$, has been substituted for E_k. This is, strictly speaking, incorrect, because the energy of the system contains exchange terms in addition to the kinetic energy of the electrons. Hence, actually[8]

$$E_k=\hbar^2(k^2-k_m{}^2)/2m$$
$$+(e^2/2\pi k)(k^2-k_m{}^2)\ln|(k+k_m)/(k-k_m)| \qquad (15a)$$

should be substituted for E_k in (15). (The energy is normalized in (15a) in such a way that it vanishes for $k=k_m$). The second term of (15a) is unimportant in insulators, since there the energy denominator will contain a finite term (the energy gap between the zones), compared with which the second term of (15a) is negligible. However, in a metal, the second term of (15a) is actually more important than the first one, because it predominates in the region $k\sim k_m$ which gives the largest contribution to the summation. If one wants to be quite sure that the summation gives a divergent result, one must substitute (15a) for (15) and carry out the summation. This can be done, but the calculation is not given here in detail. If the summation is replaced in the usual way by integration, the integrand is an expression the leading term of which, in the neighborhood of $x=0$, is $(x\ln x)^{-1}dx$. This integral diverges, although the divergence is much weaker than that of $x^{-1}dx$ which is obtained if the second term[9] in (15a) is neglected. This means that, strictly speaking, the second approximation gives an energy correction which is, per electron, proportional to $\ln\ln n$ rather than to $\ln n$. Although this is not a very bad divergence, it shows, nevertheless, that the Schrödinger perturbation theory becomes increasingly worse for metals as the number of particles increases.

3. THE ELECTRON INTERACTION IN INSULATORS

In order to introduce the gap in energy found in insulators into the matrix elements of electrostatic interaction used to calculate the second-order term in the energy of the electrons, a method due to Peierls[5] will be followed. Because of Bragg reflection of the lattice waves by the crystal, the first-order wave functions are degenerate. Therefore a linear combination of first-order wave functions must be used. These may be obtained by modifying the plane waves, with the period of the whole crystal, by waves with the period of the lattice constant. Here only two waves will be used which correspond to values of the wave vector in the two lowest zones. The normal state is represented by the

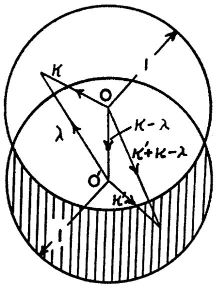

FIG. 2. **κ'** is to be integrated throughout the cross-hatched volume. **κ** and **κ**−**λ** lie inside the sphere with its center at 0. **κ'**+**κ**−**λ** lies outside this sphere. **κ'** lies inside and **λ** outside the sphere with its center at 0'.

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[7] I am grateful to Dr. Conyers Herring for a discussion of this case.

[8] P. A. M. Dirac, Proc. Camb. Phil. Soc. **26**, 376 (1930). Also L. Brillouin, J. de phys. et rad. **3**, 565 (1932) and J. Bardeen, Phys. Rev. **49**, 653 (1936).

[9] I am very much indebted to Professor John Bardeen for pointing out to me that it is necessary to include the exchange term when the calculation is carried out for the metal.

wave vector **k** in the first zone combined with that for which the x component is k_x-2k_m. The y and z components are the same. Waves with $\mathbf{k}'$ and y component $k_y'-2k_m$ are combined for the other occupied state. Similarly the x components of the two wave vectors of one excited electron differ by $2k_m$ and the y components of the other excited electron differ by $2k_m$. The vectors for a simple cubic lattice are shown in Fig. 1 together with points which correspond to the wave vectors with which they are combined. It will be seen that these vectors satisfy the requirement (12) that $\mathbf{k}+\mathbf{k}'=\mathbf{l}+\mathbf{l}'$ or $l_x-k_x=k_x'-l_x'$, $l_y-k_y=k_y'-l_y'$, $l_z-k_z=k_z'-l_z'$. The z components are all equal.

Thus for the normal electrons

$$\begin{aligned}\psi_k&=(1/V^{\frac{1}{2}})\{\cos\tfrac{1}{2}\beta\exp[i\mathbf{k}\cdot\mathbf{r}_1]+\sin\tfrac{1}{2}\beta\exp[i\mathbf{k}\cdot\mathbf{r}_1-2k_mx_1)],\\ \psi_{k'}&=(1/V^{\frac{1}{2}})\{\cos\tfrac{1}{2}\beta'\exp[i\mathbf{k}'\cdot\mathbf{r}_2]+\sin\tfrac{1}{2}\beta'\exp[i(\mathbf{k}'\cdot\mathbf{r}_2-2k_my_2)]\}\end{aligned}\tag{16a}$$

and for the excited electrons

$$\begin{aligned}\psi_l&=(1/V^{\frac{1}{2}})\{\cos\tfrac{1}{2}\gamma\exp[i\mathbf{l}\cdot\mathbf{r}_1]+\sin\tfrac{1}{2}\gamma\exp[i(\mathbf{l}\cdot\mathbf{r}_1-2k_mx_1)]\},\\ \psi_{l'}&=(1/V^{\frac{1}{2}})\{\cos\tfrac{1}{2}\gamma'\exp[i\mathbf{l}'\cdot\mathbf{r}_2]+\sin\tfrac{1}{2}\gamma'\exp[i(l'\cdot r_2-2k_my_2)]\}.\end{aligned}\tag{16b}$$

The energy corresponding to ψ_k is

$$E_k=(\hbar^2/2m)[k^2\cos^2\tfrac{1}{2}\beta+(k^2-4k_xk_m+4k_m^2)\sin^2\tfrac{1}{2}\beta]-2\sin\tfrac{1}{2}\beta\cos\tfrac{1}{2}\beta\eta\tag{17}$$

$$=(\hbar^2/2m)[k^2+2k_m(k_m-k_x)(1-\cos\beta)]-\eta\sin\beta,\tag{18}$$

where

$$\eta=\int P'e^{\pm 2k_mx_1}dx_1dy_1dz_1$$

is the first Fourier coefficient of the periodic lattice potential, P'. Similar expressions hold for $E_{k'}$, E_l and $E_{l'}$. β is now chosen to make E_k a minimum

$$\eta\cos\beta=\frac{\hbar^2}{m}k_m(k_m-k_x)\sin\beta,\tag{19}$$

$$\tan\beta=\frac{m\eta}{\hbar^2k_m(k_m-k_x)},\tag{20}$$

$$\tan\left(\frac{\pi}{2}-\beta\right)=\cot\beta=\frac{\hbar^2k_m(k_m-k_x)}{m\eta}\tag{21}$$

from which

$$\beta=\tfrac{1}{2}\pi-\hbar^2k_m(k_m-k_x)/m\eta\text{ approximately.}\tag{22}$$

Similarly

$$\beta'=\frac{\pi}{2}-\frac{\hbar^2k_m(k_m-k_y')}{m\eta},\quad\gamma=-\frac{\pi}{2}+\frac{\hbar^2k_m(l_x-k_m)}{m\eta},\quad\gamma'=-\frac{\pi}{2}+\frac{\hbar^2k_m(l_y'-k_m)}{m\eta},\tag{23}$$

so that

$$\frac{\beta-\gamma}{2}=\frac{\pi}{2}-\frac{\hbar^2k_m(l_x-k_x)}{2m\eta},\quad\frac{\beta'-\gamma'}{2}=\frac{\pi}{2}-\frac{\hbar^2k_m(l_y'-k_y')}{2m\eta}.\tag{24}$$

The wave functions may be substituted in (9) and the matrix elements $V_{\mathbf{kk}'\mathbf{ll}'}$ calculated. Only those four, of the possible products, for which k_m cancels out in the exponent give elements different from zero. Identical integrals as given in (12) are obtained for each of these four products. With the values of these integrals from (14), the matrix elements of (9) become

$$V_{\mathrm{kk'll'}}=-(\cos\tfrac{1}{2}\beta\cos\tfrac{1}{2}\gamma\sin\tfrac{1}{2}\beta\sin\tfrac{1}{2}\gamma+\cos\tfrac{1}{2}\beta\sin\tfrac{1}{2}\beta'\cos\tfrac{1}{2}\gamma\sin\tfrac{1}{2}\gamma'+\sin\tfrac{1}{2}\beta\cos\tfrac{1}{2}\beta'\sin\tfrac{1}{2}\gamma\cos\tfrac{1}{2}\gamma'$$

$$+\sin\tfrac{1}{2}\beta\sin\tfrac{1}{2}\beta'\cos\tfrac{1}{2}\gamma\cos\tfrac{1}{2}\gamma')\frac{4\pi e^2}{V}\frac{1}{|\mathbf{l}-\mathbf{k}|^2}\delta(\mathbf{k}+\mathbf{k}'-\mathbf{l}-\mathbf{l}') \tag{25}$$

$$=-\cos\frac{\beta-\gamma}{2}\cos\frac{\beta'-\gamma'}{2}\frac{4\pi e^2}{V}\frac{1}{|\mathbf{l}-\mathbf{k}|^2}\delta(\mathbf{k}+\mathbf{k}'-\mathbf{l}-\mathbf{l}') \tag{26}$$

$$=\frac{\pi e^2\hbar^4 k_m^2}{Vm^2\eta^2}\frac{(l_x-k_x)(l_y-k_y)}{|\mathbf{l}-\mathbf{k}|^2}\delta(\mathbf{k}+\mathbf{k}'-\mathbf{l}-\mathbf{l}'), \tag{27}$$

where, for the last line, (24) has been used. As the matrix elements are complicated, (4) is difficult to integrate. It may be seen that the maximum value of $(l_x-k_x)(l_y-k_y)/|l-k|^2$ is $\frac{1}{2}$, so that the maximum value of the matrix element is $\pi e^2\hbar^4k_m^2/2Vm^2\eta^2$. This is the value when $l=k$, i.e. on the boundary of the first Brillouin zone. For large values of l, the matrix element is given by (14). Hence an approximation which is valid at $l=k$ and large l is

$$V_{\mathrm{kk'll'}}=\frac{4\pi e^2}{V}\frac{\delta(\mathbf{k}+\mathbf{k}'-\mathbf{l}-\mathbf{l}')}{|\mathbf{l}-\mathbf{k}|^2+8m^2\eta^2/\hbar^4k_m^2}. \tag{28}$$

(4) will now give the second-order term in the energy. The energy difference between the normal and excited electrons may be found from (18).

$$E_0-E_l=(\hbar^2/2m)[k^2+2k_m(k_m-k_x)(1-\cos\beta)+k'^2+2k_m(k_m-k_y)(1-\cos\beta')-l^2$$

$$-2k_m(k_m-l_x)(1-\cos\gamma)-l'^2-2k_m(k_m-l_y)(1-\cos\gamma')]$$

$$-\eta(\sin\beta+\sin\beta'-\sin\gamma-\sin\gamma') \tag{29}$$

$$=-(\hbar^2/m)(\mathbf{l}-\mathbf{k})\cdot(\mathbf{l}-\mathbf{k}')-4\eta, \tag{30}$$

since on the boundary of the first Brillouin zone where $l_x=l_y=k_x=k_y=k_m$, (23) shows that $\beta=\beta'=\pi/2$, $\gamma=\gamma'=-\pi/2$. This is a valid approximation since it is only for small values of E_0-E_l that the terms in the energy sum of (4) are large, and E_0-E_l is smallest on the boundary. Therefore

$$E=\textstyle\sum_l(E_0-E_l)|a_l|^2=-\sum_{\mathrm{kk'l}}\dfrac{16\pi^2e^4m}{V^2\hbar^2(|\mathbf{l}-\mathbf{k}|^2+8m^2\eta^2/\hbar^4k_m^2)^2[(\mathbf{l}-\mathbf{k})\cdot(\mathbf{l}-\mathbf{k}')+4m\eta/\hbar^2]}. \tag{31}$$

This value of the energy reduces to (15) for metals if $\eta=0$, i.e., when there is no periodic lattice field. In order to carry out the summation of (31), the simple cube of Fig. 1 will be replaced by a sphere of radius k_m. The sum over the wave vectors is then replaced by integration over $\mathbf{k}$ and $\mathbf{k}'$ inside, and over $\mathbf{l}$ and $\mathbf{l}'$ outside this sphere. The change from sum to integral gives a factor $V^3/(2\pi)^9$. Let

$$A=-16\pi^2e^4mV/\hbar^2(2\pi)^9,\quad \alpha=8m\eta/\hbar^2k_m^2, \tag{32}$$

then

$$E=A\int\frac{d\mathbf{k}d\mathbf{k}'d\mathbf{l}}{(|\mathbf{l}-\mathbf{k}|^2+\alpha^2k_m^2/8)^2[(\mathbf{l}-\mathbf{k})\cdot(\mathbf{l}-\mathbf{k}')+\alpha k_m^2/2]}. \tag{33}$$

The integration of (33) may be simplified by setting k_m equal to 1, and integrating with the unit sphere as the boundary of the occupied states. This may be done by setting

$$\boldsymbol{\kappa}=\mathbf{k}/k_m,\quad \boldsymbol{\kappa}'=\mathbf{k}'/k_m\quad\text{and}\quad \boldsymbol{\lambda}=\mathbf{l}/k_m, \tag{34}$$

which gives

$$E=Ak_m{}^3\int\frac{d\boldsymbol{\kappa}d\boldsymbol{\kappa}'d\boldsymbol{\lambda}}{(|\boldsymbol{\lambda}-\boldsymbol{\kappa}|^2+\alpha^2/8)^2[(\boldsymbol{\lambda}-\boldsymbol{\kappa})\cdot(\boldsymbol{\lambda}-\boldsymbol{\kappa}')+\alpha/2]}. \tag{35}$$

There are three cases to be considered:

$$\text{(a) } |\boldsymbol{\lambda}-\boldsymbol{\kappa}|\leq 1,\quad \text{(b) } 1\leq|\boldsymbol{\lambda}-\boldsymbol{\kappa}|\leq 2,\quad \text{and}\quad \text{(c) } 2\leq|\boldsymbol{\lambda}-\boldsymbol{\kappa}|. \tag{36}$$

The integration will be carried out for case (a) first with respect to $\boldsymbol{\kappa}'$. Let

$$|\boldsymbol{\lambda}-\boldsymbol{\kappa}|=a,\quad 2\boldsymbol{\lambda}\cdot(\boldsymbol{\lambda}-\boldsymbol{\kappa})=b^2,\quad \text{and}\quad |\boldsymbol{\kappa}'+\boldsymbol{\kappa}-\mathbf{1}|=c. \tag{37}$$

Then

$$2\boldsymbol{\kappa}'\cdot(\boldsymbol{\lambda}-\boldsymbol{\kappa})=\kappa'^2+a^2-c^2\quad \text{and}\quad b^2=\lambda^2+a^2-\kappa^2. \tag{38}$$

$\boldsymbol{\kappa}$ is a vector to points inside a sphere of radius 1 in Fig. 2. $\boldsymbol{\kappa}-\boldsymbol{\lambda}$ will also be a vector inside the same sphere since $|\boldsymbol{\lambda}-\boldsymbol{\kappa}|\leq 1$. $\boldsymbol{\lambda}$, however, must be a vector lying outside a sphere of radius 1. This second sphere may be drawn with $\boldsymbol{\kappa}-\boldsymbol{\lambda}$ as a center. From the end of $\boldsymbol{\kappa}-\boldsymbol{\lambda}$, $\boldsymbol{\kappa}'$ will be a vector lying inside the second sphere. Finally since $\boldsymbol{\lambda}'=(\boldsymbol{\kappa}'+\boldsymbol{\kappa}-\boldsymbol{\lambda})$ must be a vector lying outside the sphere containing $\boldsymbol{\kappa}$, the volume of integration for $\boldsymbol{\kappa}'$ is outside the first sphere and inside the second, and is shown cross hatched in Fig. 2. Using for $\boldsymbol{\kappa}'$ elliptic coordinates κ' and c with the volume element $2\pi\kappa' d\kappa' cdc/a$ gives for the part of (35) depending on $\boldsymbol{\kappa}'$

$$\begin{aligned}&\frac{4\pi}{a}\int_{1-a}^{1}\kappa' d\kappa'\int_{1}^{\kappa'+a}\frac{cdc}{b^2+c^2-a^2+\alpha-\kappa'^2}\\ &\quad=(\pi/4a^3)\{[4a^2-(b^2+\alpha)^2]\ln(2a+b^2+\alpha)+4a^2(b^2+\alpha-a^2)\ln(b^2+\alpha-a^2)\\ &\quad+(b^2+\alpha+2a-2a^2)(b^2+\alpha-2a-2a^2)\ln(b^2+\alpha+2a-2a^2)+2a^2(b^2+\alpha+2a-a^2)\}=f(b^2+\alpha,a).\end{aligned} \tag{39}$$

For $1\leq|\boldsymbol{\lambda}-\boldsymbol{\kappa}|\leq 2$, (39) becomes

$$\frac{4\pi}{a}\left(\int_0^{a-1}\kappa' d\kappa'\int_{a-\kappa'}^{a+\kappa'}\frac{cdc}{b^2+c^2-a^2+\alpha-\kappa'^2}+\int_{a-1}^{1}\kappa' d\kappa'\int_{1}^{a+\kappa'}\frac{cdc}{b^2+c^2-a^2+\alpha-\kappa'^2}\right)=f(b^2+\alpha,a) \tag{40}$$

as before. For $2\leq|\boldsymbol{\lambda}-\boldsymbol{\kappa}|$

$$\begin{aligned}&\frac{4\pi}{a}\int_0^1\kappa' d\kappa'\int_{a-\kappa'}^{a+\kappa'}\frac{cdc}{b^2+c^2-a^2+\alpha-\kappa'^2}\\ &\quad=(\pi/4a^3)\{[4a^2-(b^2+\alpha)^2][\ln(b^2+\alpha+2a)-\ln(b^2+\alpha-2a)]+4a(b^2+\alpha)\}=g(b^2+\alpha,a).\end{aligned} \tag{41}$$

Thus

$$E=Ak_m{}^3\int\frac{d\mathbf{k}d\boldsymbol{\lambda}}{(a^2+\alpha^2/8)^2}[f(b^2+\alpha,a)+g(b^2+\alpha,a)], \tag{42}$$

where f is used for $0\leq a\leq 2$ and g for $2\leq a$.

The integration with respect to $\boldsymbol{\lambda}$ must be carried out outside the sphere O' of Fig. 2. Using elliptic coordinates a and λ again gives

$$\begin{aligned}E=2\pi Ak_m{}^3\int\frac{d\boldsymbol{\kappa}}{\kappa}\Bigg\{&\int_{1-\kappa}^{1+\kappa}\frac{ada}{(a^2+\alpha^2/8)^2}\int_1^{a+\kappa}f(b^2,a)\lambda d\lambda+\int_{1+\kappa}^{2}\frac{ada}{(a^2+\alpha^2/8)^2}\int_{a-\kappa}^{a+\kappa}f(b^2,a)\lambda d\lambda\\ &+\int_2^{\infty}\frac{ada}{(a^2+\alpha^2/8)^2}\int_{a-\kappa}^{a+\kappa}g(b^2,a)\lambda d\lambda\Bigg\}.\end{aligned} \tag{43}$$

Now let

$$\int f(b^2, a)\lambda d\lambda = F(\kappa, \lambda), \quad \int g(b^2, a)\lambda d\lambda = G(\kappa, \lambda). \tag{44}$$

Then

$$E = 2\pi A k_m{}^3 \int \frac{d\kappa}{\kappa} \left\{ \int_{1-\kappa}^{1+\kappa} \frac{ada}{(a^2+\alpha^2/8)^2} [F(\kappa, a+\kappa) - F(\kappa, 1)] \right.$$
$$\left. + \int_{1+\kappa}^{2} \frac{ada}{(a^2+\alpha^2/8)^2} [F(\kappa, a+\kappa) - F(\kappa, a-\kappa)] + \int_{2}^{\infty} \frac{ada}{(a^2+\alpha^2/8)^2} [G(\kappa, a+\kappa) - G(\kappa, a-\kappa)] \right\}. \tag{45}$$

The integration with respect to κ is next carried out within the unit sphere.

$$E = 8\pi^2 A k_m{}^3 \left\{ \int_0^1 \frac{ada}{(a^2+\alpha^2/8)^2} \int_{1-a}^{1} \kappa d\kappa [F(\kappa, a+\kappa) - F(\kappa, 1)] \right.$$
$$+ \int_1^2 \frac{ada}{(a^2+\alpha^2/8)^2} \int_{a-1}^{1} \kappa d\kappa [F(\kappa, a+\kappa) - F(\kappa, 1)]$$
$$+ \int_1^2 \frac{ada}{(a^2+\alpha^2/8)^2} \int_{0}^{a-1} \kappa d\kappa [F(\kappa, a+\kappa) - F(\kappa, a-\kappa)]$$
$$\left. + \int_2^\infty \frac{ada}{(a^2+\alpha^2/8)^2} \int_{0}^{1} \kappa d\kappa [G(\kappa, a+\kappa) - G(\kappa, a-\kappa)] \right\}. \tag{46}$$

Finally let

$$F_1(\kappa, a) = \int [F(\kappa, a+\kappa) - F(\kappa, 1)]\kappa d\kappa,$$
$$F_2(\kappa, a) = \int [F(\kappa, a+\kappa) - F(\kappa, a-\kappa)]\kappa d\kappa, \tag{47}$$
$$G_1(\kappa, a) = \int [G(\kappa, a+\kappa) - G(\kappa, a-\kappa)]\kappa d\kappa,$$

which gives for the energy

$$E = 8\pi^2 A k_m{}^3 \left\{ \int_0^1 \frac{ada}{(a^2+\alpha^2/8)^2} [F_1(1, a) - F_1(1-a, a)] \right.$$
$$\left. + \int_1^2 \frac{ada}{(a^2+\alpha^2/8)^2} [F_1(1, a) + F_2(a-1, a) - F_1(a-1, a)] + \int_2^\infty \frac{ada}{(a^2+\alpha^2/8)^2} G_1(1, a) \right\}, \tag{48}$$

since $F_2(0, a) = 0$ and $G_1(0, a) = 0$. Now it turns out that

$$F_1(1, a) - F_1(1-a, a) = F_1(1, a) + F_2(a-1, a) - F_1(a-1, a) \tag{49}$$

so that the energy becomes

$$E = 8\pi^2 A k_m{}^3 \left\{ \int_0^2 \frac{ada}{(a^2+\alpha^2/8)^2} [F_1(1, a) - F_1(1-a, a)] + \int_2^\infty \frac{ada}{(a^2+\alpha^2/8)^2} G_1(1, a) \right\}. \tag{50}$$

The integrals of (47) have been evaluated by elementary integration and depend on a and α. The integrals were divided into two parts, those containing logarithms and those containing polynomials only. The latter were integrated except for certain terms which it was convenient to combine with the logarithmic integrals to prevent their becoming too large to integrate graphically. This gives E in the form

$$\begin{aligned}
E=A\frac{k_m{}^3\pi^3}{60}\Bigg\{\int_0^2 &\frac{da}{4a^4(a^2+\alpha^2/8)^2}\{2(4a+\alpha)^3(-16a^2+12a\alpha-\alpha^2)\ln(4a+\alpha)\\
&+(2a^2+4a+\alpha)^3[16a^2-12a(\alpha+2a^2)+(\alpha+2a^2)^2]\ln(2a^2+4a+\alpha)\\
&+(-2a^2+4a+\alpha)^3[16a^2-12a(\alpha-2a^2)+(\alpha-2a^2)^2]\ln(-2a^2+4a+\alpha)\\
&+20a^2(a^2+2a+\alpha)^3(-a^2+6a-\alpha)\ln(a^2+2a+\alpha)\\
&+20a^2(-a^2+2a+\alpha)^3(-a^2-6a+\alpha)\ln(-a^2+2a+\alpha)+80a^4\alpha^3\ln\alpha\}\\
&+\{-256-16\alpha+(3\sqrt{2}-\tfrac{3}{4})\alpha^2+(\alpha^2+32)^{-1}(\tfrac{3}{4}\alpha^4-8\alpha^3+232\alpha^2-1280\alpha+1536)\\
&+169\sqrt{2}\tan^{-1}(4\sqrt{2}/\alpha)+(232+3\alpha^2/2)\ln(\alpha^2+32)/\alpha^2\}\\
&+\int_2^\infty\frac{da}{4a^4(a^2+\alpha^2/8)^2}\Big\{(2a^2+\alpha)^3[(2a^2+\alpha)^2-80a^2]\ln[1-16a^2/(2a^2+\alpha)^2]\\
&+64a^3[16a^2-5(2a^2+\alpha)^2]\ln\frac{1+4a/(2a^2+\alpha)}{1-4a/(2a^2+\alpha)}+128a^8\Big\}\\
&+4\{4\sqrt{2}[3+(56/\alpha)+(128/\alpha^2)][\tfrac{1}{2}\pi-\tan^{-1}(4\sqrt{2}/\alpha)]+32/\alpha\\
&\qquad\qquad-32(\alpha^2+32)^{-1}[-3\alpha-32+(160/\alpha)]\}\Bigg\}. \qquad (51)
\end{aligned}$$

If in (51) $\alpha=0$, then the value of the energy as given by (15) for metals may be evaluated. The integration may be carried out and gives

$$E=Ak_m{}^3(\pi^3/3)\{-32[1-(\tfrac{1}{5})\ln 2]\lim_{a\to 0}\ln a-(32/5)(\ln 2)^2-(448/15)\ln 2+4\pi^2-204/5\}, \qquad (52)$$

which is logarithmically infinite as has been mentioned in Section 2.

The integrals still remaining in (51) were evaluated graphically for $\eta=\hbar^2k_m{}^2/2m$, $\hbar^2k_m{}^2/4m$, and $\hbar^2k_m{}^2/8m$. These values of η correspond to gaps between the first and second Brillouin zones equal to twice, once, and one-half of the energy width of the first zone, respectively. From (32) the corresponding values of α are 4, 2 and 1. The integrand for $\alpha=0$ at $a=40$ differed by only 12 percent from that for $\alpha=2$, and was approaching it. The integral from 40 to ∞ made up 40 percent of the result. Therefore the integrals from $a=40$ to ∞ were computed for all values of α by setting $\alpha=0$.

The energy is thus made up of a series of terms

$$E=Ak_m{}^3(\pi^3/60)\left\{\left[\int_0^2+\int_2^{40}+\int_{40}^\infty\right](\text{logarithmic terms})+\left[\int_0^2+\int_2^\infty\right](\text{other terms})\right\} \qquad (53)$$

$$=Ak_m{}^3(\pi^3/60)(-509.28-366.36-17.58+539.00+399.12) \qquad (54)$$

for $\alpha=2$. From (32), $A=-16\pi^2e^4mV/h^2(2\pi)^9=V/16\pi^7$ if the energy is to be in Rydberg units. If r_s is defined by $V=(4/3)\pi r_s{}^3 2n$ where $2n$ is the number of electrons, then $k_m{}^3=9\pi/4r_s{}^3$ and

$$E=-(4/3)(\pi r_s{}^3/16\pi^7)(9\pi/4r_s{}^3)\pi^3 0.748=-0.0142\text{ Ry} \qquad (55)$$

per electron.

Thus the following values of the energy have been obtained:

$$\begin{aligned} \alpha=1, \quad & E=-0.0394 \text{ Ry} \\ \alpha=2, \quad & E=-0.0142 \text{ Ry} \\ \alpha=4, \quad & E=-0.0073 \text{ Ry}. \end{aligned} \tag{56}$$

The correlation energy as given in (35) depends only on $\alpha=8m\eta/h^2k_m{}^2$ rather than on both η and k_m since V which occurs in A is inversely proportional to $k_m{}^3$. This shows that (35) cannot be quite correct, because the correlation energy will be independent of η when η is very small, but will still depend on k_m. This is, of course, the limiting case of metals where, as shown in Section 2, the method breaks down. Again if k_m is very small, i.e., r_s very large, the correlation energy should approach zero, because the whole electrostatic energy (the partial absence of which is represented by the correlation energy) goes to zero. This is not manifest in (35) or (54).

Wigner[2] gives $-0.58/(r_s+5.1)$ Ry as the correlation energy. If $r_s=4$ Bohr units is taken as a reasonable value, this gives -0.064 Ry so that the values in (56) are of the same order of magnitude. The values in (56) are nevertheless somewhat smaller than the -0.045 Ry estimated by Wigner to be correct. This is reasonable because one would expect the correlation energy to increase further with decreasing η even if it did not increase as drastically (to infinity) as (52) for this limiting case indicates.

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A Determination of the Elastic Modulus s_{13} of Beta-Quartz

A. W. LAWSON
Randal Morgan Laboratory of Physics, University of Pennsylvania, Philadelphia, Pennsylvania

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The adiabatic Young's modulus of beta-quartz along a direction at 45 degrees to the optic axis has been measured as a function of temperature. These data, in conjunction with that of Atanasoff and Kammer, and of Perrier and de Mandrot, yield a value for the adiabatic elastic modulus s_{13} of beta-quartz equal to -0.226×10^{-12} cm²/dyne at 600°C and indicate that the value reported by Osterberg and Cookson for c_{44} is inconsistent with the stability of beta-quartz.

The crystal structure of beta-quartz is hexagonal holoaxial.[1,2] In virtue of the particular symmetry characteristic of such a structure, beta-quartz may be piezoelectric. The possible nonvanishing components of the piezoelectric tensor expressed in Voigt's[3] notation are:

$$\begin{matrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{matrix}$$

The fact that the piezoelectric modulus d_{14} is not evanescent has been established by Osterberg and Cookson[4] who succeeded in exciting shear vibrations in beta-quartz by applying an alternating electric field parallel to an axis of diagonal symmetry (X axis). From a knowledge of the fundamental frequency of free vibration of a thin crystal plate and the dimensions and density of the plate, Osterberg and Cookson, employing a theory analogous to that developed by Mason,[5]

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