NATURAL COORDINATES FOR ELECTRONS IN SOLIDS

The adage that solving a physics problem is a question of finding the right coordinate system is demonstrated for electrons in crystals. Coordinates that reflect the regularity of the crystal greatly simplify the problem.

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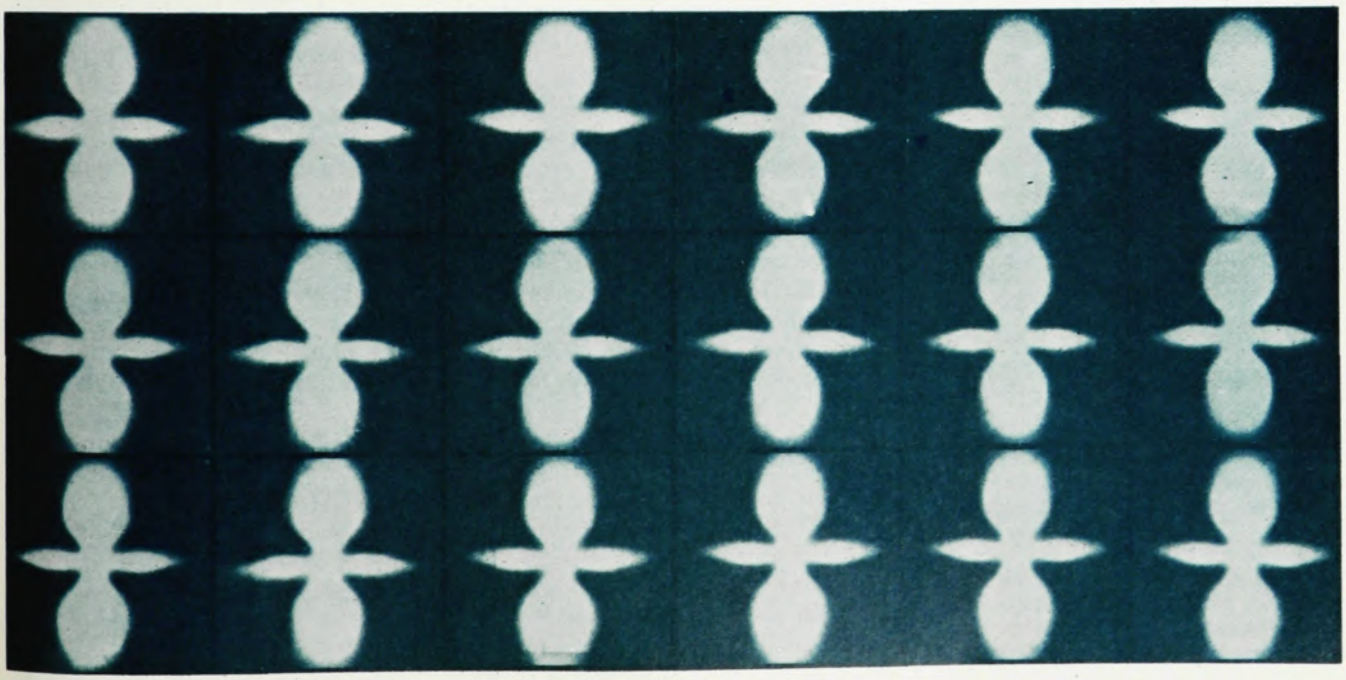
THE DESCRIPTION OF A PROBLEM in physics can often be significantly simplified by a suitable choice of coordinates. Usually the choice of the best coördinates is dictated by the symmetry of the problem. Thus for a spherically symmetric potential it is most convenient to use spherical coordinates. In some cases it is very easy to choose the right coördinates; in other cases, the problem is not trivial at all. Here we will discuss the choice of suitable coördinates for the motion of electrons in solids.

One of the most fundamental properties of any solid is its periodic structure. Formally, this property is expressed by the invariance of the potential energy, $V(x)$, with respect to translations by the constant a of a unit cell

$$V(x + a) = V(x) \tag{1}$$

For many problems in solid-state physics we are interested in finding coördinates that are most appropriate for a potential with the symmetry expressed by equation 1. The reason we expect such coördinates to be useful can be seen in the example of spherical symmetry. In that case, the potential depends only on the absolute value, r, of the radius vector, $\mathbf{r}$, and by choosing spherical coördinates r, θ and φ we can separate them and so simplify the solution of the problem

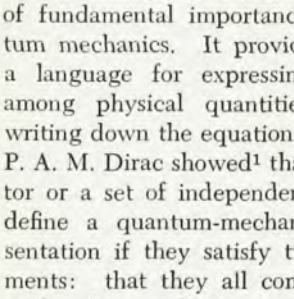


A PERIODIC POTENTIAL. "Natural" coordinates would show the same kind of symmetry as this. —FIG. 1

significantly. We expect similar simplification for motion in a periodic potential if the coördinates in which the motion is described reflect best the symmetry of the potential given in equation 1. (See figure 1.)

Microscopic motion in solids is usually treated on an atomic scale, and the description should therefore be based on quantum mechanics. There are a number of well known schemes, called *representations*, for describing motion in quantum mechanics. For example, in the x-representation the Hamiltonian of the problem is expressed as a function of x and derivatives with respect to x (the latter come from the dependence of the Hamiltonian on the momentum of the particle). Similarly, in the p representation the Hamiltonian depends on p and derivatives with respect to p.

The concept of a representation is of fundamental importance in quantum mechanics. It provides us with a language for expressing relations among physical quantities and for writing down the equations of motion. P. A. M. Dirac showed[1] that an operator or a set of independent operators define a quantum-mechanical representation if they satisfy two requirements: that they all commute with each other, and that any additional operator that commutes with all the operators of the set is necessarily a function of them. For example, the coördinate operator defines a representation in quantum mechanics. For one degree of freedom, it is the coördinate x; for three degrees of freedom, x, y and z together define a representation. In the language of quantum mechanics, the problem that we are going to discuss here is the definition of a set of coördinates (or operators that form a quantum-mechanical representation) that reflect in the closest way the symmetry of the periodic potential in equation 1.



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Quasimomentum

For an electron moving in a periodic potential, $V(x)$, Schrödinger's equation is

$$\left[\frac{p^2}{2m} + V(x)\right]\psi(x) = \epsilon\psi(x) \qquad (2)$$

The translational invariance of equation 2 can be expressed by saying that the operator

$$\mathrm{T}(a) = \exp(ipa) \qquad (3)$$

commutes with the Hamiltonian of equation 2. (We assume $h/2\pi = 1$.) This operator represents a finite translation in x space[2] by the constant a

$$\mathrm{T}(a)\psi(x) = \psi(x + a)$$

In solid-state physics the operator $\mathrm{T}(a)$ is of very great importance because it commutes with the Hamiltonian of equation 2 and is therefore a constant of motion. The eigenvalues of $\mathrm{T}(a)$ define what is called[3] the *quasimomentum k*, namely, the eigenvalues of $\mathrm{T}(a)$ are $\exp(ika)$ with k varying from 0 to $2\pi/a$. When k is given, the momentum of the electron is known within a multiple of $2\pi/a$. Being a constant of motion, k in a periodic potential plays the role of the momentum of a free particle. It is for this reason that k is so important in the dynamics of solids.

Quasicoördinate

Because k is a constant of motion, one should in general expect that the potential in equation 2 is independent of k (for example, in the case of a spherical potential the constants of the motion are functions of the angular coördinates θ and φ, on which the potential does not depend). What is the coördinate on which $V(x)$ in equation 2 depends? This question is very easy to answer. Because $V(x)$ is periodic, it clearly depends only on the position of the electron inside a unit cell of length a, but not on which of the unit cells it is. Let us denote the location of the electron inside a unit cell by q (see figure 2). It is clear that the potential in equation 2 is a function of q only, that is, $V(x) = V(q)$, because all the unit cells are identical. In full analogy with k, we shall call q the *quasicoördinate.* When q is given, the position of the electron is defined within a multiple of the constant a. Knowing this important fact, that the potential depends only on q, we are interested in finding the operator that defines q. It has to be similar in structure to the operator of equation 3 that defines k. It can be seen that the operator

$$\mathrm{T}\left(\frac{2\pi}{a}\right) = \exp\left(ix\,\frac{2\pi}{a}\right) \qquad (4)$$

has the eigenvalues

$$\exp\left(i\,q\,\frac{2\pi}{a}\right)$$

and therefore defines q, the quasicoördinate. q assumes values from 0 to a. The operator in equation 4 represents a translation in p-space, because $x = i\,\partial/\partial p$

$$\mathrm{T}\left(\frac{2\pi}{a}\right)\psi(p) = \psi\left(p - \frac{2\pi}{a}\right)$$

The definition of the quasicoördinate q is therefore completely analogous to the definition of the quasimomentum k. (See figure 2.)

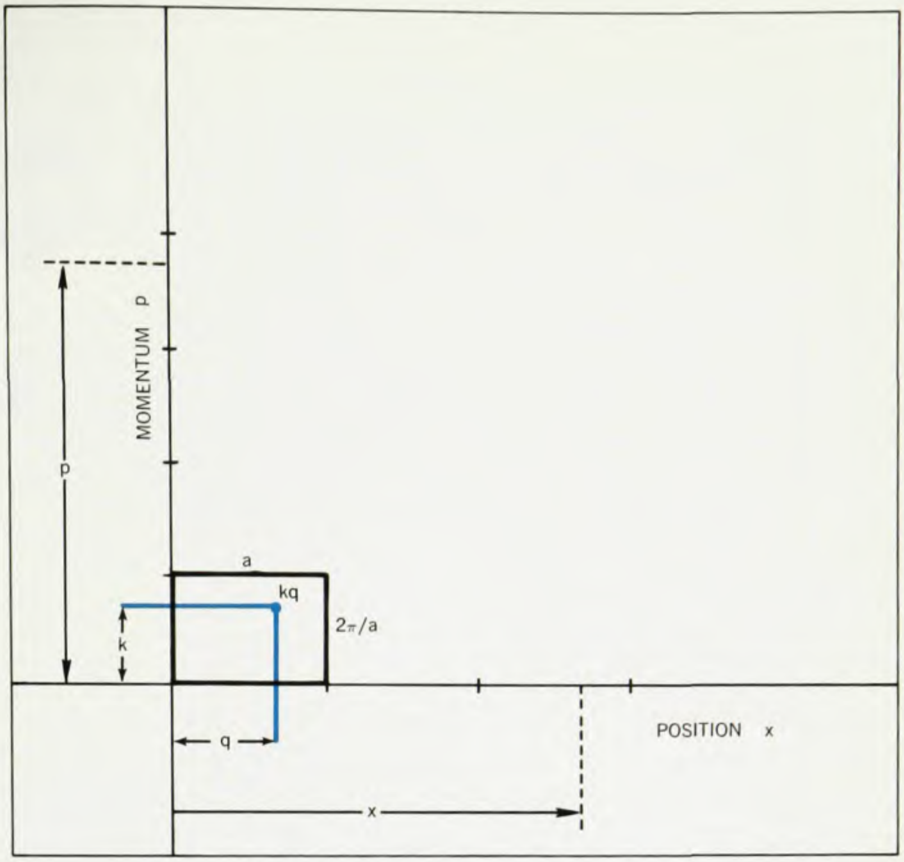
kq representation

A very important quantum-mechanical fact about the operators of equations 2 and 4 is that they commute (we know $e^Ae^B = e^Be^Ae^{[A,B]}$ for operators A and B such that $[A,B]$ commutes with both A and B)

$$\left[\mathrm{T}(a), \mathrm{T}\left(\frac{2\pi}{a}\right)\right] = 0$$

This result means that it is possible to measure the eigenvalues of $\mathrm{T}(a)$ and $\mathrm{T}(2\pi/a)$ simultaneously, or alternatively that k and q of an electron can be given together. It turns out that not only can $\mathrm{T}(a)$ and $\mathrm{T}(2\pi/a)$ be measured together, but one can also prove that these two operators form a complete set of commuting operators; that is, they define a quantum-mechanical representation.[4] We call this representation the *kq-representation*. It solves the problem of finding the coördinates that reflect the symmetry of the periodic potential of equation 1. When written in the *kq*-representation, the potential energy depends only on q, which is similar to the dependence of the spherical potential on the absolute value of r only.

The *kq*-representation has a number of interesting features. In quantum mechanics it is impossible to use the coördinate and the momentum simultaneously in a description of motion because of the uncertainty principle. The coördinate x and the momentum p can not be measured simultaneously, and the motion is usually described in either the x- or the p-representation. The kq-representation uses partial information about the momentum and the coördinate: k gives the momentum p within an additive constant $2\pi/a$ times an integer, whereas q measures the coördinate within an additive constant a times an integer. Of course, by giving k and q we have only partial information about p and x, and because the operators of equations 3 and 4 commute, the uncertainty principle is not violated in the kq-representation. k and q carry the most information one can get simultaneously about p and x.



NATURAL COORDINATES in the phase plane. On this figure the thick black lines show the unit displacement and momentum, the colored lines the position of a point kq. Then $x = q + 2a$, $p = k + 3x\ 2\pi/a$. **—FIG. 2**

Another interesting feature of the kq-representation is its connection to the Bohr-Sommerfeld quantization rules and the concept of the number of states in a unit cell in phase space. It is well known[2] that for finding energy levels one can use the condition

$$\oint p\,dx = h(n + \gamma) \qquad (5)$$

where the integration is on a closed path in phase space, n is an integer that counts the number of the quantum state, and γ is a factor between 0 and 1. Equation 5 can also be written as follows (we neglect γ)

$$\frac{\oint p\,dx}{h} = n \qquad (6)$$

The left-hand side of equation 6 can be interpreted[2] as the number of quantum states contained within the area $\oint p\,dx$ of phase space. This is the well known rule that the number of quantum states in any area of phase space is given by this area divided by h. This rule can be easily obtained by the concept of the kq representation. In this representation the area of the elementary region where k and q vary (see figure 2) is $2\pi/a \times a = 2\pi$, or h if $h/2\pi$ is not assumed to be 1. Every point in this elementary cell represents a different quantum state. In classical phase space p and x cover the whole plane. The number of times a definite quantum state appears in an area $\oint p\,dx$ of the phase space is given by this area divided by h, because every quantum state appears once in the area of the elementary cell h. We see therefore that the left-hand side of equation 6 gives the number of times a given quantum state appears in the area $\oint p\,dx$ or the *weight* of the quantum state. It is in this meaning that equation 6 is used in integration over phase space in statistical mechanics.[5] One usually replaces the classical elementary area $dp\,dx$ by $dp\,dx/h$.

Angular coordinate

In the above definition the kq representation was closely connected to a periodic structure. In fact, we looked for coördinates that reflect the symmetry of a periodic potential. It is clear, however, that the kq representation does not necessarily have to be connected to a periodic potential. The constant a in the operator of equation 3 can be chosen arbitrarily, and the corresponding operator of equation 4 will still be defined. In a crystal, a has the meaning of a unit cell constant, and $2\pi/a$ is the length of a unit cell in the reciprocal lattice. In general, the kq representation can be defined on any pair of conjugate coördinates that satisfy the same commutation relation as p and x do. For example, the z component of the angular momentum, l_z, and the angle of rotation, α, in the xy plane form conjugate coördinates. The operators that define the kq representation for the angular-momentum–angle degree of freedom will clearly be[6]

$$T(2\pi) = \exp\,(il_z 2\pi) \qquad (7)$$

$$T(1) = \exp\,(i\alpha) \qquad (8)$$

where for obvious reasons a was chosen to equal 2π (the period of α is 2π). Because l_z assumes only integral values, the operator in equation 7 is a unit operator, and $\exp\,(i\ \alpha)$ (equation 8) by itself defines a quantum-mechanical representation.

In the case of the xp-degree of freedom we had the choice of either using the x-representation, the p-representation, or the kq-representation. Arguments of convenience or simplicity would decide which of them to use. We do not have this choice in the case of the angular coördinate because the latter is by nature a quasicoördinate (defined modulo 2π), and therefore it has to be defined by means of the operator in equation 8 in order to avoid inconsistencies.[6] For example, if one uses the regular commutation relation

$$(l_z,\alpha) = -i \qquad (9)$$

one comes to an inconsistency. Let us calculate the matrix elements of equation 9 in the eigenfunctions of l_z. We have

$$(m - m')(m|\alpha|m') = -i\delta_{mm'} \qquad (10)$$

where m is the eigenvalue of l_z. Equation 10 is clearly contradictory, because for $m' = m$ the left-hand side is zero while the right-hand side equals $-i$. This inconsistency follows from the assumption that α itself is a well defined operator. As was mentioned before, α by its nature is a quasicoördinate and has to be defined by means of a periodic function of α. The operator of equation 8 is a periodic function of α, and by measuring its eigenvalues (or equivalently by measuring cos α and sin α) one measures α itself in a consistent way.[6]

Other representations

The connection between the kq representation and other representations can easily be obtained. First we find the eigenfunctions of the operators in equations 3 and 4. They are[4]

$$\psi_{kq}(x) = \sqrt{\frac{a}{2\pi}} \sum_n \exp(ikna) \times \delta(x - q - na) \qquad (11)$$

where δ is the Dirac delta function. It can be easily checked that

$$\mathrm{T}(a)\,\psi_{kq}(x) = \exp(ika)\,\psi_{kq}(x)$$

$$\mathrm{T}\left(\frac{2\pi}{a}\right)\psi_{kq}(x) = \exp\left(iq\,\frac{2\pi}{a}\right)\psi_{kq}(x)$$

This means that the $\psi_{kq}(x)$ in equation 11 are common eigenfunctions of $\mathrm{T}(a)$ and $\mathrm{T}(2\pi/\mathrm{a})$. Being eigenfunctions of a complete set of commuting operators $\mathrm{T}(a)$ and $\mathrm{T}(2\pi/a)$, the functions $\psi_{kq}(x)$ also form a complete system of functions. Any functions $\psi(x)$ can be expanded in terms of them. Thus

$$\psi(x) = \int dkdq\, C(kq)\psi_{kq}(x) \qquad (12)$$

The function $C(kq)$ is the wave function in the kq representation if $\psi(x)$ is the wave function in the x-representation. Using equation 12 one can find the basic operators x and p in the kq-representation[4]

$$x = i\frac{\partial}{\partial k} + q \qquad (13)$$

$$p = -i\frac{\partial}{\partial q} \qquad (14)$$

This completes the construction of the kq representation: We have the operators of equations 3 and 4 that define it, their common eigenfunctions (equation 11) and equations 13 and 14 for the basic operators x and p. Having this information, we can write any problem in the kq representation.

Dynamics in solids

As an example of the usefulness of the kq representation in the dynamics of electrons in solids, let us discuss Schrödinger's equation for an electron in a periodic potential and external electric **E** and magnetic **H** fields. In the **r** representation this equation is

$$\left[\frac{\left(\mathbf{p} + \frac{e}{2c}\mathbf{H} \times \mathbf{r}\right)^2}{2m} + V(\mathbf{r}) + e\mathbf{E}\cdot\mathbf{r}\right] \times \psi(\mathbf{r}) = \epsilon\psi(\mathbf{r}) \qquad (15)$$

With equations 13 and 14 in three dimensions (the generalization for three dimensions is straightforward[4]), equation 15 in the kq representation will be (we write this equation for the function $U(\mathbf{kq}) = \exp(-i\ \mathbf{k}\cdot\mathbf{q})\ C(\mathbf{kq})$; the $U(\mathbf{kq})$ corresponds to the periodic part of the Bloch function[3])

$$\left[\frac{\left(-i\frac{\partial}{\partial \mathbf{q}} + \mathbf{k} + \frac{e}{2c}\mathbf{H} \times i\frac{\partial}{\partial \mathbf{k}}\right)^2}{2m} + V(\mathbf{q}) + e\,\mathbf{E}\cdot i\frac{\partial}{\partial \mathbf{k}}\right] U(\mathbf{kq}) = \epsilon U(\mathbf{kq}) \qquad (16)$$

Equation 16 shows a number of interesting features. As we mentioned before, in the kq representation one should expect to have the variables separated to some extent. We can see this feature in equation 16. When there are no external fields the Hamiltonian contains the pure Bloch part (the motion in a periodic potential) $-1/2m\ \partial^2/\partial\mathbf{q}^2 + V(\mathbf{q})$, the free-electron part $k^2/2m$, and an interaction term between these two motions. In the external fields, the Hamiltonian separates in a similar way: There is the Bloch term, the term for the motion of a free electron (an electron without the periodic potential) in external fields and an interaction term. This feature of the separation of variables corresponds to the general behavior of electrons in crystals and simplifies significantly the description of the problem.[4,7]

Another interesting feature of equation 16 is the way the magnetic field appears in it. One can see that a very simple rule works: In order to introduce the magnetic field in the equation, **k** has to be replaced by $\mathbf{k} + e/2c\ \mathbf{H} \times i\ \partial/\partial\mathbf{k}$. This rule demonstrates that **k** in a crystal plays to some extent the same role as **p** for a free electron. It should also be pointed out that equation 16 gives a very convenient starting equation for the derivation of effective Hamiltonians in a magnetic field.[4]

As a final example of the usefulness of equation 16, let us consider the acceleration theorem for an electron in a periodic potential and an external electric field. This theorem is very simple[3]

$$\dot{\mathbf{k}} = -e\mathbf{E} \qquad (17)$$

The usual derivation of it requires, however, rather complicated algebra. In the k representation, the acceleration theorem (equation 17) follows straightforwardly from Schrödinger's equation (equation 16) with $H = 0$. One need only use the simple quantum-mechanical rule that the time rate of change of **k** is given by the commutator of the Hamiltonian and **k**

$$\dot{\mathbf{k}} = i[H,\mathbf{k}] = -e\mathbf{E}$$

The simplicity of the last derivation and of the examples mentioned before show the usefulness of the kq representation in describing the motion of electrons in crystals. As we expected, the kq representation simplifies the description considerably. Because k and q best reflect the symmetry of the periodic potential, they should be called the *natural coördinates* for dynamics in solids.

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References

1. P. A. M. Dirac, *The Principles of Quantum Mechanics*, Oxford University Press, New York, N.Y. (1958).
2. L. D. Landau, E. M. Lifshitz, *Quantum Mechanics*, Pergamon Press, London (1958).
3. C. Kittel, *Quantum Theory of Solids*, John Wiley & Sons, New York, N.Y. (1963).
4. J. Zak, Phys. Rev. Lett. **19**, 1385 (1967); Phys. Rev. **168**, 686 (1968).
5. L. D. Landau, E. M. Lifshitz, *Statistical Physics*, Pergamon Press, London (1958).
6. J. Zak, Physics Letters (to be published); Phys. Rev. (to be published).
7. J. Zak, Phys. Rev. **177**, 1151 (1969). □