Calculation of exchange corrections for a crystal

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An asymptotic expression for the wave function near a tunneling path is obtained for a classical crystal with weak anharmonicities. A general expression is deduced for the exchange integral, including the preexponential factor. The phonon-spin Hamiltonian is obtained for a crystal composed of Fermi atoms. The spin-phonon vertex found in this way is large compared with that for conventional magnetic materials.

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Quantum crystals are currently the subject of intensive theoretical and experimental studies. The most striking quantum property of such crystals is the possibility of tunneling of atoms located near various sites in the crystal lattice. Fairly rough calculations of the exchange integral for He^3 are reported in [1,2]. The importance of these calculations lies in the conclusion that the exchange governs the magnetic properties of crystalline He^3.

We shall show how such effects in a hypothetical almost "classical" crystal with weak anharmonicities can be considered in the main order of u_0/a, where u_0 is the amplitude of zero-point vibrations and a is the lattice constant. An important difference from the earlier calculations is our allowance for the interaction of spins with lattice vibrations, which differs considerably from the case of ordinary electronic magnetic materials.

Quantum tunneling in a metastable crystal accompanied by the formation of a nucleus is considered in the paper of one of the present authors [3] and by I. M. Lifshitz and Yu. M. Kagan. [4] An improvement of the method of [3] employed in the present study makes it possible, in particular, to calculate more exactly the relevant probability.

The potential energy of a classical crystal in the configuration space has—in addition to a minimum corresponding to the position of all atoms at some lattice sites—similar minima corresponding to the transpositions of atoms between the same sites. In a classical crystal, these minima are separated by a barrier which is assumed to be impermeable.

Our aim is to find corrections associated with the finite permeability of the barrier. The main contribution is made by transpositions between the nearest neighbors and we shall confine our treatment to this case; we shall assume that the corrections can be added independently of each transposition. The problem is, to some extent, analogous to the one-dimensional case of a particle in a two-well potential satisfying the classical conditions. However, there is an important difference which is associated with the multi-dimensional nature of our problem and the proximity of the second well, which corresponds to the transposition of just two particles, whereas the ordinates of the other particles are assumed to be unaffected and the dependence of the wave function on these coordinates remains essentially unchanged.

1. WAVE FUNCTION OF A CRYSTAL IN THE QUASICLASSICAL APPROXIMATION

In this section, we shall find an asymptotic expression for the wave function of the whole crystal on the assumption that the number of atoms N is finite and we shall make the transition to the limit $N \to \infty$ only in the final formulas. When tunneling takes place, the main contribution comes from regions where the potential energy is much greater than the average energy of zero-point vibrations per particle. This allows us to use the quasiclassical approximation for the wave function of a crystal:

$$\Psi = A \exp(-S/\hbar), \tag{1.1}$$

where the action S is found as the solution of the Hamilton–Jacobi equation with zero energy (the action is purely imaginary because the range in question is inaccessible to the classical treatment):

$$\frac{1}{2m}\left(\frac{\partial S}{\partial \mathbf{x}_i}\right)^2 = U(\mathbf{x}_1, \ldots, \mathbf{x}_N). \tag{1.2}$$

For simplicity, we shall assume that all atoms in our crystal are identical; U is the potential energy of the crystal. We shall be interested in the tunneling process in the configuration space of the crystal from a point $\mathbf{X}^{(1)} = (\mathbf{x}_1^0, \mathbf{x}_2^0, \ldots, \mathbf{x}_N^0)$, corresponding to the minimum of U, to a symmetric point $\mathbf{X}^{(2)} = (\mathbf{x}_2^0, \mathbf{x}_1^0, \ldots, \mathbf{x}_N^0)$, corresponding to the transposition of atoms 1 and 2.

Integration of Eq. (1.2) is equivalent to the finding of trajectories, i.e., of solutions of a system of ordinary differential equations

$$m\frac{d^2\mathbf{x}_i}{dt^2} = \frac{\partial U}{\partial \mathbf{x}_i}, \tag{1.3}$$

and these trajectories emerge from the point $\mathbf{X}^{(1)}$, where $\{\mathbf{x}_i\} = \mathbf{X}^{(1)}$ in the limit $t \to -\infty$, and the action along such a trajectory is given by

$$S = 2m\int_{-\infty}^{t} U(\mathbf{x}_1(t), \ldots, \mathbf{x}_N(t))\,dt, \tag{1.4}$$

since at the point $\mathbf{X}^{(1)}$ itself the action S should vanish, as found in the harmonic approximation.

We can easily verify that the equilibrium point $\mathbf{X}^{(1)}$ is a node at which an infinite number of trajectories begins, so that the formula (1.4) can be used to find the action at any point in space reached by the trajectories in question.

Among the trajectories beginning from $\mathbf{X}^{(1)}$, there are those which terminate at $\mathbf{X}^{(2)}$. We shall call a trajectory of this kind a tunneling path between $\mathbf{X}^{(1)}$ and $\mathbf{X}^{(2)}$. We shall be interested in the action near such a tunneling path because this action governs the tunneling probability. Clearly, only a small number of atoms actually travels along a tunneling path. In our case, these are the two atoms being transposed and their nearest neighbors, so that the displacement $\mathbf{x}_i$ falls rapidly with rising i. Bearing this point in mind, we can find adjacent

trajectories by linearizing the equations of motion and assuming that

$$x_i(t)=\xi_i(t)+u_i(t),$$

where $\xi_i(t)$, satisfying the system (1.3), govern the tunneling path so that the quantities $u_i(t)$ are the solutions of the equations

$$m\frac{d^2u_i}{dt^2}=\frac{\partial^2U}{\partial x_i\,\partial x_j}\Big|_{\xi(t)}u_j(t). \tag{1.5}$$

These equations correspond to the harmonic approximation for particles far from those being transposed, whereas, in the case of those close to the transposed particles, the potential energy can be considered in the anharmonic approximation.

The system (1.5) has 3N independent solutions $v_{in}(t)$, which vanish in the limit $t=-\infty$ (the trajectories should start from the point $X^{(1)}$), so that an unrestricted solution is

$$u_i(t)=\sum_{n\neq 0}c_nv_{in}(t), \tag{1.6}$$

where c_n are constants. The solution corresponding to a displacement of the tunneling path with time is excluded:

$$v_{i0}(t)=\dot{\xi}_i(t). \tag{1.7}$$

It follows from the system (1.5) that

$$\frac{d}{dt}[\dot{v}_{in}(t)v_{in'}(t)-v_{in}(t)\dot{v}_{in'}(t)]=0$$

and, consequently, since $v_{in}\to 0$ in the limit $t\to-\infty$,

$$\dot{v}_{in}(t)v_{in'}(t)=v_{in}(t)\dot{v}_{in'}(t). \tag{1.8}$$

The action in the vicinity of the point $\xi(t_0)$ in the tunneling path can easily be expressed in terms of the solution matrix v_{in}. We find that

$$S=\int_0^x\frac{\partial S}{\partial x_i}dx_i=\int_0^{\xi(t_0)}\frac{\partial S}{\partial\xi_i}d\xi_i+\int_{\xi(t_0)}^x\frac{\partial S}{\partial x_i}dx_i,$$

since the integral is independent of the path. Hence,

$$S=S(t_0)+m\int_{\xi(t_0)}^x[\dot{\xi}_i(t)+\dot{u}_i(t)]\,dx_i,\quad \frac{\partial S}{\partial x_i}=m\dot{x}_i.$$

A displacement of the point x from $\xi(t_0)$ alters the constants c_n and the time $t=t_0+\delta t(x)$. Retaining terms to the second order inclusive, we obtain

$$S=S(t_0)+m\dot{\xi}_i(t_0)[x_i-\xi_i(t_0)]+\int_{\xi(t_0)}^x[\ddot{\xi}_i(t_0)\,\delta t(x)+\dot{u}_i(t_0)]\,dx_i.$$

We shall integrate along a path which corresponds to the smallest change in the constants c_n and we shall assume that $c_0=\delta t(x)$. Clearly, a suitable selection of c_n and c_0 allows us to reach any point x since the system of equations

$$x_i-\xi_i(t_0)=\Delta x_i=\sum_{n=0}^{3N}c_nv_{in}(t_0)$$

has a determinant which does not vanish because of the linear independence of the solutions v_{in}. Thus,

$$S=S(t_0)+m\dot{\xi}_i(t_0)\Delta x_i+m\int_0^c c_{n'}\dot{v}_{in'}(t_0)v_{in}(t_0)\,dc_n,$$

and, in accordance with (1.8), the last integral is independent of the path. Finally, using $c_n=v_{ni}^{-1}(t_0)\Delta x_i$ ($v_{i'n}v_{ni}^{-1}=\delta_{ii'}$), we find that

$$S=S(t_0)+m\dot{\xi}_i(t_0)\Delta x_i+\tfrac{1}{2}S_{ij}(t)\Delta x_i\Delta x_j,\qquad S_{ij}(t)=m\dot{v}_{in}(t)v_{nj}^{-1}(t), \tag{1.9}$$

where the indices i are labels of the particles and of the Cartesian coordinates.

The formula (1.9) represents the action in a small region $\xi_i(t_0)$ in a tunneling path. However, if $\Delta x_i\xi_i(t_0)=0$, the same formula represents, in fact, the action S over the whole of a hyperplane perpendicular to the tunneling path at $t=t_0$, which is due to the fact that only small harmonic displacements need to be allowed for in the case of distant atoms. The cross sections of such hyperplanes are of little importance to us because we are concerned with the region where $\Delta x_i\sim u_0$ (u_0 is the amplitude of the zero-point vibrations) and the radius of curvature of a tunneling path is of the order of the lattice constant $a\gg u_0$.

We can determine the coefficient A in the expression (1.1) by deducing from the Schrödinger equation the following exact equation:

$$-\frac{\hbar^2}{2m}\frac{\partial^2A}{\partial x_i^2}+\frac{\hbar}{m}\frac{\partial S}{\partial x_i}\frac{\partial A}{\partial x_i}+\left(\frac{\hbar}{2m}\frac{\partial^2S}{\partial x_i^2}-E\right)A=0. \tag{1.10}$$

In the one-dimensional case, the quantity $(\hbar^2/2m)\partial^2A/\partial x_i^2$ can be ignored because it gives rise to corrections of the order of $(\hbar^2/U^2a^2m)^{1/2}\ll 1$ at high values of U (i.e., in the quasiclassical limit). This is generally untrue in the many-dimensional quasiclassical case because the harmonic approximation applies to the distant transposed atoms and because in considering the excited states (i.e., phonons), we should include all powers in the Hermite polynomial occurring in A and not just the highest order.

However, we can obtain an approximate (in respect of the quasiclassical parameter) solution on the assumption that

$$\begin{aligned}A&=A_{n_{ks}}+A_{n_{ks}-2}+\ldots+A_0, && \text{if } n_{ks} \text{ is even},\\ A&=A_{n_{ks}}+A_{n_{ks}-2}+\ldots+A_1, && \text{if } n_{ks} \text{ is odd}.\end{aligned} \tag{1.11}$$

($E=E_0+n_{\mathbf{k}_S}\hbar\omega_{\mathbf{k}_S}$, where $\omega_{\mathbf{k}_S}$ is the frequency of a phonon of momentum $\mathbf{k}$ and polarization s).

The quantities $A_{n_{\mathbf{k}_S}}$ are defined by recurrence relationships, exactly as can be done in the case of the Hermite polynomials:

$$\frac{\hbar}{m}\frac{\partial A_{n_{ks}}}{\partial x_i}\frac{\partial S}{\partial x_i}+\left(\frac{\hbar}{2m}\frac{\partial^2S}{\partial x_i^2}-E_0-\hbar\omega_{ks}n_{ks}\right)A_{n_{ks}}=0, \tag{1.12}$$

$$\frac{\hbar}{m}\frac{\partial A_{n_{ks}-2}}{\partial x_i}\frac{\partial S}{\partial x_i}+\left(\frac{\hbar}{2m}\frac{\partial^2S}{\partial x_i^2}-E_0-\hbar\omega_{ks}n_{ks}\right)A_{n_{ks}-2}=\frac{\hbar^2}{2m}\frac{\partial^2A_{n_{ks}}}{\partial x_i^2}. \tag{1.13}$$

Differentiation of the last terms in Eq. (1.11) gives terms which are small in respect of the quasiclassical parameter and the series can be truncated.

The solution of (1.12) can easily be obtained by assuming $A_{n_{\mathbf{k}_S}}=A_SA_E$, where

$$\begin{aligned}&\frac{\hbar}{m}\frac{\partial A_S}{\partial x_i}\frac{\partial S}{\partial x_i}+\left(\frac{\hbar}{2m}\frac{\partial^2S}{\partial x_i^2}-E_0\right)A_S=0,\\ &\frac{\hbar}{m}\frac{\partial A_S}{\partial x_i}\frac{\partial S}{\partial x_i}=\hbar\frac{dA_E}{dt}=\delta EA_E,\qquad \delta E=n_{ks}\hbar\omega_{ks}.\end{aligned} \tag{1.14}$$

We can easily show (see, for example, [5]) that the determinant $\Delta=|\partial x_i/\partial c_j|$, where $x_i(t, c_j)$ are the solutions of the system

$$\frac{dx_i}{dt}=\frac{1}{m}\frac{\partial S}{\partial x_i},$$

satisfies the equation

$$\frac{\hbar}{m}\frac{\partial\Delta}{\partial x_i}\frac{\partial S}{\partial x_i}=\frac{\hbar}{m}\frac{\partial^2S}{\partial x_i^2}\Delta.$$

The solutions $x_i(t, c_j)$ are of the form

$$x=\xi_i(t+c_0)+\sum_{n\neq 0} c_n v_{in}(t+c_0),$$

so that the determinant is

$$\Delta=\begin{vmatrix}\dot{\xi}_i\\ v_{in}\end{vmatrix}+\sum_{n'} c_{n'}\begin{vmatrix}\dot{v}_{in'}\\ v_{in}\end{vmatrix}.$$

The second term can be ignored because it is a small quantity, of the order of u_0/a, compared with the first term, i.e., we can consider Δ only on a singular trajectory. The first determinant is easily calculated and we can express the solution A_S in the form

$$A_s=\exp\int_{-\infty}^{t}\left(\frac{1}{2m}S_{ii}(t)-\frac{E_0}{\hbar}\right)dt.$$

The solution (1.14) is found equally readily and we obtain

$$A_{n_{ks}}(t)=A^0_{n_{ks}}\exp\left(n_{ks}\omega_{ks}t+\int_{-\infty}^{0}\left[\frac{S_{ii}(t)}{2m}-\frac{E_0}{\hbar}\right]dt\right).$$

The constant $A^0_{n_{ks}}$ is found from the condition that, in the limit $t=-\infty$, our solution should reduce to the wave function in the harmonic approximation

$$\Psi=H_{n_{ks}}(q_{ks})\exp\left(-\frac{1}{2\hbar}S_{ij}^0\Delta x_i\Delta x_j\right),$$

$$q_{ks}=\frac{1}{N^{1/2}}\sum_i e^{i\mathbf{k}\mathbf{R}_i}(\mathbf{x}_i-\mathbf{R}_i)\mathbf{e}_{ks}$$

($\mathbf{e}_{ks}$ is a unit vector of the phonon polarization, N is the number of unit cells in a crystal, S^0_{ij} is the matrix S_{ij} in the harmonic approximation). Hence, we readily obtain

$$A_{n_{ks}}(t)=\lim_{t\to-\infty}\left\{e^{i\mathbf{k}\mathbf{R}_i}\left[(\xi_i(t)-\mathbf{R}_i)+\Delta\mathbf{x}_i(t)\right]\frac{\mathbf{e}_{ks}}{N^{1/2}}\right\}^{n_{ks}}\nu_{ks}$$

$$=\lim_{t\to-\infty}e^{n_{ks}\omega_{ks}t}A^0_{n_{ks}},$$

or

$$A^0_{n_{ks}}=\nu_{ks}(N^{-1/2}B_{ks}+\beta_{ks})^{n_{ks}},$$

where

$$B_{ks}=\lim_{t\to-\infty}\sum_i(\xi_i(t)-\mathbf{R}_i)\exp(-\omega_{ks}t+i\mathbf{k}\mathbf{R}_i)\mathbf{e}_{ks},$$

$$\beta_{ks}=\lim_{t\to-\infty}\frac{1}{N^{1/2}}e^{-\omega_{ks}t}\sum_{in}v_{in}(t)\,e^{i\mathbf{k}\mathbf{R}_i}\mathbf{e}_{ks}c_n$$

(ν_{ks} is a constant normalization coefficient).

The following comments should be made about these formulas. The equations for

$$\zeta_{ks}(t)=\frac{1}{N^{1/2}}\sum_{in}\mathbf{e}_{ks}v_{in}(t)\,c_n e^{i\mathbf{k}\mathbf{R}_i}$$

are of the form

$$\frac{d^2\zeta_{ks}}{dt^2}=\omega_{ks}^2\zeta_{ks}+\frac{1}{N}\sum_{k's'}\delta\omega^2_{ks;k's'}\zeta_{k's'}$$

($\delta\omega_{ks;k's'}$ is bounded in the limit $N\to\infty$).

The great majority of the trajectories corresponds to a random selection of β_{ks}, so that the second term on the right-hand side is vanishingly small on these trajectories (in the limit $N\to\infty$). Since our aim is to calculate the integrals on a hypersurface perpendicular to a tunneling path, we can ignore the difference between ζ_{ks} and the harmonic normal coordinates on the assumption that

$$\beta_{ks}e^{\omega_{ks}t}\approx\zeta_{ks}=\frac{1}{N^{1/2}}\sum_{in}\mathbf{e}_{ks}v_{in}(t)\,e^{i\mathbf{k}\mathbf{R}_i}=\frac{1}{N^{1/2}}\sum_i\mathbf{e}_{ks}\Delta\mathbf{x}_i\exp(i\mathbf{k}\mathbf{R}_i). \quad (1.15)$$

The quantities ζ_{ks} correspond to some rotation of the axes at the point $\xi_i(t)$ and can be used to calculate the Laplacian because $\partial^2/\partial x_i^2=\partial^2/\partial\zeta^2_{ks}$. Using this circumstance, we can see that differentiation of $A_{n_{ks}}$ in Eq. (1.13) reduces the power of $N^{-1/2}B_{ks}e^{\omega_{ks}t}+\zeta_{ks}$ by 2. Consequently, the solution of (1.13) becomes

$$A_{n_{ks-2}}=\nu_{n_{ks-2}}\left(\frac{1}{N^{1/2}}B_{ks}e^{\omega_{ks}t}+\zeta_{ks}\right)^{n_{ks-2}}\exp\int_{-\infty}^{t}\left[\frac{1}{2m}S_{ii}(t)-\frac{E_0}{\hbar}\right]dt,$$

where $\nu_{n_{ks-2}}$ is a new normalization coefficient deduced from the Hermite polynomial in the harmonic approximation.

Collecting in this way all the terms in (1.11), we finally obtain

$$A(E_0+\hbar\omega_{ks}n_{ks},\Delta x_i)=H_{n_{ks}}\left(\frac{1}{N^{1/2}}B_{ks}e^{\omega_{ks}t}+\zeta_{ks}\right)$$
$$\times\exp\int_{-\infty}^{t}\left[\frac{1}{2m}(S_{ii}(t)-S_{ii}^0)\,dt\right], \quad (1.16)$$

if we use $E_0=\hbar S_{ii}/2m$.

The following comments should be made on the above formula. We find that $B_{ks}/N^{1/2}\sim a/N^{1/2}\ll 1$, where a is of the order of the sum of the displacements of atoms along a tunneling path. Naturally, the expression for A also contains other terms of the order of $N^{-1/2}$; in particular, they may arise from terms of the type dropped from the determinant Δ and from allowance for various anharmonicities. However, the important point is that all these corrections are free of the factor a since they are related to various effects in a hyperplane perpendicular to a tunneling path. A correction associated with B_{ks} is the largest and gives rise to curves of the order of $N^{-1}(a/u_0)^2$ in the integrals or, if allowance is made for all the transpositions, to terms of the order of $(a/u_0)^2$.

If there are several phonons, the asymptotic form of the wave function is obtained using Eqs. (1.1), (1.9), and (1.16):

$$\Psi^0\approx\prod_{ks}H_{n_{ks}}\left(\frac{B_{ks}}{N^{1/2}}e^{\omega_{ks}t}+\zeta_{ks}\right)$$
$$\times\exp\left[\frac{1}{2m}\int_{-\infty}^{t}(S_{ii}(t)-S_{ii}^0)\,dt-\frac{S_0(t)}{\hbar}-\frac{1}{2\hbar}S_{ij}(t)\Delta x_i\Delta x_j\right]. \quad (1.17)$$

The formula (1.17) for the asymptotic form of the wave function near any tunneling path remains approximately valid until the occupation numbers become so large that we cannot ignore the difference between ζ_{ks} and $\beta_{ks}\exp(\omega_{ks}t)$.

Thus, the asymptotic wave function is obtained by finding a tunneling path and solving a system of linear equations (1.5) governing the matrix $S_{ij}(t)$. The solution of these equations and the method of determination of the matrix $S_{ij}(t)$ are considered in the Appendix.

The formula (1.17) can be used, in principle, to calculate the preexponential factor in the formula for the probability of a quantum process of formation of a nucleus of a new phase.[3]

2. CALCULATION OF MATRIX ELEMENTS

The expression (1.17) gives the asymptotic form of the wave function corresponding to the stationary state of a crystal in a region near a tunneling path. If we are interested in transposition effects, then a tunneling path

corresponds to the transposition of any two atoms in a crystal. Since the state with transposed atoms is in no way different from the initial state, we have a similar asymptotic form on moving away from any other well (with transposed atoms). Thus, if the atoms are fermions, we may assume that

$$\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N;\sigma_1,\ldots,\sigma_N)=\sum_{P,\lambda}(-1)^P c_\lambda P\Psi_\lambda^0(\mathbf{x}_1,\ldots,\mathbf{x}_N;\sigma_1,\ldots,\sigma_N), \quad (2.1)$$

where P represents the transposition of atoms (coordinates and spins) and λ is the number of stationary states in one well.

The expression (2.1) corresponds to the case when reflections from various wells are neglected. In the region near the bottom of a well, it describes the wave function of an ordinary crystal and, in the region between the wells, it gives the correct asymptote which is generated by damped waves emerging independently from each of the wells. According to Eq. (2.1), a wave function can be represented by a superposition of stationary wave functions from each of the wells. (A set of stationary states in one well is complete but ineffective because the asymptotic wave function which decreases away from one well rises on approach to another well.) The approximation of wave functions by these combinations is considered by Herring. [6]

We shall now consider a specific well. We shall draw all the tunneling paths from this well and construct hyperplanes which are perpendicular to these tunneling paths and which halve the paths. This generates a polyhedron Ω surrounding the well in question. Multiplying the stationary Schrödinger equation

$$(H-E)\Psi=0$$

by $\Psi_\rho^{0*}(\mathbf{x}_1, \ldots, \mathbf{x}_N; \sigma_1, \ldots, \sigma_N)$ and integrating with respect to Ω, we obtain

$$\int_\Omega \Psi_\rho^{0*}[(H-E)\Psi]d\Omega+\left(-\frac{\hbar^2}{2m}\right)\oint(\Psi_\rho^{0*}\nabla\Psi-\Psi\nabla\Psi_\rho^{0*})d\Sigma=0,$$

where the surface integral is taken over the hypersurface segments surrounding Ω.

The function Ψ_ρ^0 satisfies the Schrödinger equation inside Ω:

$$H\Psi_\rho=E_\rho\Psi_\rho,$$

if we assume E_ρ to be a level corresponding to some continuation of the potential outside Ω in the case when there are no other wells (i.e., in the absence of reflection). Since E_ρ differs little from the true values of E and since the overlap between Ψ_λ and $P\Psi_\lambda$ is small, we find—ignoring the terms which are quadratic in respect of the overlap—

$$(E_j-E)c_j=\frac{\hbar^2}{2m}\sum_{\rho P}\oint(\Psi_\rho^*\nabla P\Psi_j-P\Psi_j\nabla\Psi_\rho^*)d\Sigma(-1)^P c_j. \quad (2.2)$$

The nondiagonal terms $\Psi_\rho^{0*}\nabla\Psi_j^0-\Psi_j^0\nabla\Psi_\rho^{0*}$ will be ignored since they make a contribution in respect of u_0/a which is smaller than the terms left in (2.2); moreover, we shall ignore the difference between Ω and the whole space in the volume integral and we shall regard Ψ_ρ as normalized.

In the surface integral, we need retain only those transpositions which concern the nearest neighbors and, moreover, near each tunneling path, it is sufficient to allow only for the overlap of two wave functions corresponding to wells at the beginning and end of the path. In general several equivalent (in the sense of the value of the action) tunneling paths emerge from each well and reach another well. If particles cannot travel closer than the radius of a hard atomic nucleus, this must take place because the trajectories along which a particle i and a particle j are traveling (we are considering the transposition $i \rightleftarrows j$) are not identical and, consequently, there are two tunneling paths differing in respect of the transposition of the trajectories of the particles i and j. In finding the asymptote of the wave function and moving away from a symmetric well, we are traveling along the other end of the tunneling path which, considered as a path from a symmetric well, corresponds to the transposition of the trajectories of particles i and j in the initial path. Consequently, the quantities B_{ks} and S_{ij} are different for the asymptotes of the wave function in the initial and symmetric wells near the points on the same tunneling path. Therefore, we shall use (+) to denote the quantities defined along a tunneling path moving from the initial well and we shall use (−) for the corresponding quantities defined along the same tunneling path moving from a symmetric well.

Applying the transposition operator representation of spin variables, [7]

$$P_{ij}^\sigma=1/2(1+\hat\sigma_i\hat\sigma_j),$$

where $\hat\sigma$ are the Pauli matrices, we obtain

$$(E_\lambda-E)c_\lambda(\sigma)=-\frac{1}{2}\sum_{ij}(1+\hat\sigma_i\hat\sigma_j)V_{ij}^{\lambda\rho}c_\rho(\sigma) \quad (2.3)$$

[we have introduced here the spin functions $c_\lambda(\sigma)$ including in c the spin part of the wave function], where the summation over i and j extends only to the nearest neighbors. As expected, Eq. (2.3) gives the usual Heisenberg Hamiltonian. According to Eqs. (2.2) and (1.17), the quantities $V_{ij}^{\lambda\rho}$ are exponentially small and are given by

$$V_{ij}^{\lambda\rho}=\hbar\alpha_{ij}\oint\prod_{n^\lambda}H_{n_{ks}^\lambda}\left(\frac{B_{ks}^{(+)}}{N^{1/2}}+\zeta_{ks}\right)\prod_{n^\rho}H_{n_{ks}^\rho}\cdot\left(\frac{B_{ks}^{(-)}}{N^{1/2}}+\zeta_{ks}\right)$$
$$\times\exp\left[\frac{1}{m}\int_{-\infty}^{0}(\tilde S_{ll}^{(ij)}(t)-S_{ll}^0)\,dt-\frac{1}{\hbar}S_0(\infty)-\frac{1}{\hbar}\tilde S_{lk}^{(ij)}\Delta x_l\Delta x_k\right]\dot x(0)\,d\Sigma,$$

where we are asusming that Σ intersects a tunneling path at t = 0, $S_0(\infty)$ is the total change in the action along the tunneling path, and α_{ij} is the number of equivalent tunneling paths in the transposition $i \rightleftarrows j$. The matrix $\tilde S_{lk}^{(ij)}(t)=1/2(S_{lk}^{(+)}+S_{lk}^{(-)})$, and the method for the calculation of its eigenvalues and the corresponding traces are all given in the Appendix.

We can replace the variables Δx_i with the variables ζ_{ks} in Eq. (1.15) by rotating the coordinates and assuming that integration takes place over the whole space; this can be done if we introduce a factor $\delta(\nu_i\Delta x_i)$, where $\nu=\dot x(0)/\dot x(0)$ is a unit vector of the tangent to the tunneling path. In the new representation, the elements of the matrix $\tilde S_{lk}^{(ij)}(0)$ differ from the elements of the harmonic matrix (which is diagonal in this representation) only by quantities of the order of 1/N. In calculating a small number of integrals with respect to ζ_{ks} including the Hermite polynomials $H_{n_{ks}}(B_{ks}/N^{1/2}+\zeta_{ks})$, we can ignore this difference because it gives rise to terms of the order of 1/N without a large factor of the order of $(a/u_0)^2$. Integration with respect to other varia-

bles corresponding to the remaining degrees of freedom must be carried out allowing for this difference but the presence of the factors $H_{n_{ks}}$ can be ignored.

The necessary integrations give the following expressions for the diagonal elements

$$V_{ij}^{\lambda\lambda}=\hbar\dot{x}_{ij}(0)\alpha_{ij}\exp\Big[-\frac{S_0(\infty)}{\hbar}+\frac{1}{m}\int_{-\infty}^{t}[\tilde{S}_{ll}^{(ij)}(t)-S_{ll}^{0}]dt$$

$$-\frac{1}{2}\sum_m\ln\frac{\Lambda_m^{(ij)}(0)}{\Lambda_m^{0}}\Big]\prod_{k_s}\Big(1+\frac{2n_{k_s}B_{k_s}^{(+)}B_{k_s}^{(-)}}{Nu_{k_s}^{2}}\Big)\sum_m\Big(\frac{\pi\nu_m^{2}}{\Lambda_m^{2}}\Big)^{-1/2}, \quad (2.4)$$

$$u_{k_s}=[\hbar/(m\omega_{k_s})]^{1/2},$$

or, if we go over to the limit $N\to\infty$, we find that

$$\prod_{k_s}\Big(1+\frac{2n_{k_s}B_{k_s}^{(+)}B_{k_s}^{(-)}}{Nu_{k_s}^{2}}\Big)=\exp\Big(2\int_{V_B}n_{k_s}\frac{B_{k_s}^{(+)}B_{k_s}^{(-)}}{u_{k_s}^{2}}\frac{d^3k}{V_B}\Big), \quad (2.5)$$

where V_B is the volume of a unit cell in the lattice. The quantities $\Lambda_m^{(ij)}(0)$ are the eigenvalues of the matrix $\tilde{S}_{lk}^{(ij)}(t)$ (the upper indices denote the tunneling path).

The expression (2.4) is valid as long as the occupation numbers of phonons are not very large so that only a small number of states is occupied,

$$\sum n_{k_s}\ll N,$$

which limits its usefulness in thermodynamic calculations to low temperatures.

Similar calculations can also be carried out for nondiagonal elements $V_{ij}^{\lambda\rho}$. However, it is important to note that these quantities are exponentially small and, moreover they contain the factor $N^{-1/2}$ because of the orthogonality of the Hermite polynomials for $B_{ks}=0$. Thus, in the case of transitions involving a change in n_{ks} by unity, we obtain

$$V_{ij}^{n^\mu,n^\mu+1}=\frac{2^{1/2}(B_{k_s}^{(+)}+B_{k_s}^{(-)})}{2N^{1/2}u_{k_s}}J_{ij}(\{n_\mu\})\sqrt{n_{k_s\mu}+1},$$

where

$$J_{ij}(\{n_\mu\})=\hbar\dot{x}^{(ij)}(0)\Big(\sum_m\frac{\pi\nu_m}{\Lambda_m^{2}}\Big)^{-1/2}\exp\Big[-\frac{S_0}{\hbar}+\frac{1}{m}\int_{-\infty}^{0}(\tilde{S}_{ll}^{(ij)}(t)-S_{ll}^{0})dt$$

$$-\frac{1}{2}\sum_m\ln\frac{\Lambda_m^{(ij)}(0)}{\Lambda_m^{0}}+\sum_{s'}\Big(\int_{V_B}n_{k's'}^{\mu}\frac{2B_{k's'}^{(+)}B_{k's'}^{(-)}}{V_Bu_{k's'}^{2}}d^3k'\Big)\Big].$$

Hence, we can see that the nondiagonal elements can be ignored since the corrections associated with them are of the second order in respect of the overlap of the wave functions although the phonon levels are, in fact, continuous and the gaps between them are much smaller than the corrections due to the exchange interaction.

The results obtained can be expressed in the form of the effective phonon–spin Hamiltonian

$$H=\sum\hbar\omega_{k_s}a_{k_s}^{+}a_{k_s}+\sum_{ij}J_{ij}(0)\exp\Big(\sum_s\int_{V_B}\frac{2B_{k_s}^{(+)}B_{k_s}^{(-)}n_{k_s}}{V_Bu_{k_s}^{2}}d^3k\Big)$$

$$\times\frac{1}{2}(1+\hat{\sigma}_i\hat{\sigma}_j)\Big(1+\sum_{k,s}\frac{B_{k_s}^{(+)}+B_{k_s}^{(-)}}{2^{1/2}u_{k_s}}(a_{k_s}+a_{k_s}^{+})\Big). \quad (2.6)$$

The quantity $(B_{ks}^{(+)}+B_{ks}^{(-)})/2^{1/2}u_{ks}$ acts as an effective phonon-spin vertex. It follows from Sec. 1 that $B_{ks}^{(ij)}$ is described by the Fourier component of a tunneling path. A calculation of $B_{ks}^{(ij)}$ for low values of k can be carried out in the adiabatic approximation and it is then found that $B_{ks}^{(ij)}$ tends to a constant value in the limit $k\to 0$ so that the spin–phonon interaction vanishes as $k^{1/2}$, exactly as for a conventional magnetic material. A strong interaction occurs only in the range of large values of k or with optical phonons.

Since Eq. (2.6) is, in fact, the usual Heisenberg Hamiltonian representing an antiferromagnet, the various physical quantities can be calculated employing standard formulas. If the interaction with phonons is significant, it can be allowed for by replaicng n_k with $\bar{n}_k$, which gives rise to a temperature dependence of the exchange integral J. The Hamiltonian (2.6) can also be used to find corrections to the phonon spectra because of the exchange effects and, in particular, to calculate the change in the phonon frequencies in a magnetic field.

The formula for the asymptote of the wave function (1.17) can be employed to calculate the probabilities of various tunnel processes in a crystal to within the main terms in the preexponential part provided we know the tunneling path and the difference between the eigennumbers of the matrix $\tilde{S}_{lk}^{(ij)}(t)$ and their values in the harmonic limit. A tunneling path can be found and the eigenvalues can be determined by numerical calculations for some specific interaction between atoms.

In the case of solid He^3, in which the exchange (transposition) effects should be greatest, there is an additional difficulty. Although the main contribution to the calculation of the exchange integral is due to the range in which the zero-point vibration energy is much less than the potential energy and the quasiclassical approach remains valid, the equilibrium positions at the lattice sites become unstable and the harmonic approximation does not apply near the bottom of a well. Clearly, this difficulty can be avoided by introducing some self-consistent effective field near the bottom of the well, as is done, for example, in the calculation of the phonon spectra.

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APPENDIX

In the Appendix, we shall use two sets of indices: the index $\mathbf{R}$ labels the unit cells and the index $\sigma=(x, y, z)$ labels the direction of displacement of an atom in a cell. The equation (1.5) is rewritten in the form

$$\frac{d^2}{dt^2}u_{\sigma\mathbf{R}}^{(\varkappa)}(t)=\sum_{\sigma'\mathbf{R}'}G_{\sigma\mathbf{R};\sigma'\mathbf{R}'}^{(\varkappa)}(t)u_{\sigma'\mathbf{R}'}^{(\varkappa)}(t), \quad (A.1)$$

where

$$G_{\sigma\mathbf{R};\sigma'\mathbf{R}'}^{(\varkappa)}(t)=\frac{1}{m}\frac{\partial^2U(\mathbf{x})}{\partial x_{\sigma\mathbf{R}}\partial x_{\sigma'\mathbf{R}'}}\Big|_{\mathbf{x}=\xi^{(\varkappa)}(t)}.$$

The additional index $\varkappa$ represents the direction of motion along a tunneling path. If the motion along such a path begins from a point $\mathbf{X}^{(1)}$, then $\varkappa=(+)$. If $\varkappa=(-)$, the motion occurs along the same path but it begins from the point $\mathbf{X}^{(2)}$ (in the limit $t=-\infty$, we have $\xi^{(+)}=\mathbf{X}^{(1)}$, $\xi^{(-)}=\mathbf{X}^{(2)}$). In both cases, the system (A.1) has 3N independent solutions $v_{in}(t)$ which vanish in the limit $t=-\infty$.

At any given moment, the matrix $G^{(\varkappa)}(t)$ is identical

with the force matrix of small lattice vibrations with a distortion governed by the value of $\xi^{(\kappa)}(t)$. It should be noted that this structure distortion decreases rapidly away from the pair of atoms which undergoes transition. Therefore, we may assume that the distortion of the force matrix is localized within a certain region $\{L\}$. If, for example, the interaction between atoms localized at the points $\mathbf{R}_1$ and $\mathbf{R}_2$ is distorted, the force matrix should be supplemented by a term of the type

$$(\delta_{RR_1}-\delta_{RR_2})(\delta_{R'R_1}-\delta_{R'R_2})D^{(\kappa)}_{\sigma\sigma'}(t).$$

The time dependence of the real symmetric 3×3 matrix $D^{(\kappa)}_{\sigma\sigma'}(t)$ is governed by six independent matrix elements and, consequently, can be represented in the form

$$D^{(\kappa)}_{\sigma\sigma'}(t)=\sum_{m=1}^{6} a^{(\kappa)}_m(t)\,l^{(m)}_\sigma l^{(m)}_{\sigma'}.$$

If we now use the representation of plane waves, which are the eigenfunctions of the force matrix of an ideal lattice (1.15) and if we sum over all the pairs within the region $\{L\}$, we find that

$$\frac{d^2}{dt^2}\zeta^{(\kappa)}_{ks}(t)=\omega_{ks}{}^2\zeta^{(\kappa)}_{ks}(t)+\frac{1}{N}\sum_{k's'}\sum_{m=1}^{r} a^{(\kappa)}_m(t)\,l^{(m)*}_{ks}\,l^{(m)}_{k's'}\zeta^{(\kappa)}_{k's'}(t), \quad (A.2)$$

where ω_{ks} are the phonon frequencies in an ideal lattice. The asterisk denotes a complex conjugate. The total number of terms r will be called the rank of the perturbation. Solutions of the system (A.2) should tend to zero in the limit $t=-\infty$.

We shall rewrite (A.2) as a system of integral equations:

$$\zeta^{(\kappa)}_{ks}(t)=\frac{1}{\omega_{ks}}\Big\{2\int_{-\infty}^{t}\mathrm{sh}[\omega_{ks}(t-t')]\sum_{m=1}^{r} l^{(m)}_{ks}\,y^{(\kappa)}_m(t')\,dt'+C^{(\kappa)}_{ks}\exp(\omega_{ks}t)\Big\}, \quad (A.3)$$

where

$$y^{(\kappa)}_m(t)=\frac{1}{2N}\sum_{k's'}a^{(\kappa)}_m(t)\,l^{(m)*}_{k's'}\zeta^{(\kappa)}_{k's'}(t).$$

The set of constants $C^{(\kappa)}_{ks}$ defines unambiguously the solution of (A.3). We shall select these constants in such a way that, at a moment $t=0$, we have

$$\zeta^{(+)}_{ks}(0)=\zeta^{(-)}_{ks}(0),$$
$$\zeta^{(+)}_{ks}(0)+\zeta^{(-)}_{ks}(0)=\omega[\zeta^{(+)}_{ks}(0)+\zeta^{(-)}_{ks}(0)], \quad (A.4)$$

where ω is a constant, which is the same for all values of $\mathbf{k}$ and s. Differentiating the system (A.3), substituting the result into (A.4), and solving for $C^{(\kappa)}_{ks}$, we obtain the values of these coefficients

$$C^{(\kappa)}_{ks}=\sum_{m=1}^{r} l^{(m)}_{ks}\Big[\int_{-\infty}^{0}\Big(\frac{\omega}{\omega-\omega_{ks}}e^{\omega_{ks}t'}-e^{-\omega_{ks}t'}\Big)y^{(\kappa)}_m(t')\,dt'$$
$$+\frac{\omega_{ks}}{\omega-\omega_{ks}}\int_{-\infty}^{0}e^{\omega_{ks}t'}y^{(-\kappa)}_m(t')\,dt'\Big]. \quad (A.5)$$

Substituting (A.5) into (A.3), multiplying term by term by $\frac{1}{2}a^{(\kappa)}_q(t)l^{(q)*}_{ks}/N$, and summing over all $\mathbf{k}$ and s, we obtain the following system of 2r homogeneous integral equations:

$$y^{(\kappa)}_q(t)=a^{(\kappa)}_q(t)\sum_{m=1}^{r}\Big\{\int_{-\infty}^{0}R_{qm}(\omega,t,t')\,y^{(\kappa)}_m(t')\,dt'$$
$$+\int_{-\infty}^{0}T_{qm}(\omega,t,t')\,y^{(-\kappa)}_m(t')\,dt'\Big\}, \quad (A.6)$$

where

$$R_{qm}(\omega,t,t')=\frac{1}{N}\sum_{ks}\frac{l^{(q)*}_{ks}l^{(m)}_{ks}}{2\omega_{ks}}\Big[\frac{\omega}{\omega-\omega_{ks}}e^{\omega_{ks}(t+t')}-e^{-\omega_{ks}|t-t'|}\Big],$$
$$T_{qm}(\omega,t,t')=\frac{1}{N}\sum_{ks}\frac{l^{(q)*}_{ks}l^{(m)}_{ks}}{2(\omega-\omega_{ks})}e^{\omega_{ks}(t+t')}.$$

The kernels $R_{qm}(\omega,t,t')$ and $T_{qm}(\omega,t,t')$ depend on ω as a parameter and the system has solutions only for certain values $\omega=\Lambda_p$. We shall use $v_{(\kappa)}(t)$ to denote the corresponding matrix of solutions. It follows for the condition (A.4) that, at $t=0$, the matrix

$$S/m=\tfrac{1}{2}[\dot v_{(+)}v^{-1}_{(+)}+\dot v_{(-)}v^{-1}_{(-)}]$$

is diagonal and Λ_p are the diagonal elements of this matrix.

The matrix $\tilde S(t)$ applies at a moment $t=0$. At any other moment t_0, a shift of the reference system gives again (A.5) but with different kernels.

The eigenvalues Λ_p form a quasicontinuous spectrum when the number of cells tends to infinity. The trace of the matrix $\tilde S(t)$ becomes infinite but, in the limit $N\to\infty$, we can calculate the difference between the traces of the matrices S(t) and S^0.

The limit $N\to\infty$ in expressions of the (A.7) type and the calculation of the difference between the traces is considered in [8,9] in the case of lattice distortions independent of time. Let us assume that the phonon frequencies of an ideal lattice have, in the vicinity of $\omega=\mu$, a sequence j-fold degenerate levels separated by gaps $\Delta\omega$. A perturbation reduces the degeneracy multiplicity by r. The split-off r eigenvalues can be found within terms which are small compared with $\Delta\omega$ in the form

$$\Lambda_p(\mu)=\mu+\Delta\omega\chi_p(\mu),\ p=1,\dots,r. \quad (A.7)$$

In the limit $N\to\infty$, the interval $\Delta\omega$ tends to zero and, consequently, for any function of the matrix F(S), we have

$$\mathrm{Tr}\,[F(S)-F(S^0)]=\lim_{N\to\infty}\sum_{\mu p}[F(\Lambda_p(\mu))-F(\mu)]=\sum_{p}\int_{0}^{\omega_{max}}F'(\mu)\chi_p(\mu)\,d\mu. \quad (A.8)$$

Integration is carried out over the whole spectrum of an ideal lattice. A set of functions $\chi_p(u)$ is obtained by substituting (A.7) into (A.6) and going to the limit. This gives the following system of integral equations

$$y^{(\kappa)}_q(t)=a^{(\kappa)}_q(t)\sum_{m=1}^{r}\Big\{\int_{-\infty}^{0}R_{qm}(\mu,t,t')\,y^{(\kappa)}_m(t')\,dt$$
$$+\int_{-\infty}^{0}T_{qm}(\mu,t,t')\,y^{(-\kappa)}_m(t')\,dt'+g_q(\mu)\nu(\mu)e^{\mu t}\Big\}, \quad (A.9)$$

where

$$R_{qm}(\mu,t,t')=\mathrm{P}\int_{0}^{\omega_{max}}\frac{I_{qm}(\mu')}{2\mu'}\Big[\frac{e^{\mu'(t+t')}}{\mu-\mu'}-e^{-\mu'|t-t'|}\Big]d\mu',$$
$$T_{qm}(\mu,t,t')=\mathrm{P}\int_{0}^{\omega_{max}}\frac{I_{qm}(\mu')}{2(\mu-\mu')}e^{\mu'(t+t')}\,d\mu',$$
$$\nu(\mu)=\frac{1}{(2\pi)^3}\sum_{s}\oint_{\omega_{ks}=\mu}\frac{d\tau}{|\nabla_k\omega_{ks}|},$$
$$I_{qm}(\mu)=\sum_{s}\oint\frac{l^{(q)*}_{ks}l^{(m)}_{ks}}{|\nabla_k\omega_{ks}|}\frac{d\tau}{(2\pi)^3},$$

where $d\tau$ is an element of the surface $\omega_{ks}=\mu$ on which integration is carried out, and

$$d_q(\mu)=\frac{1}{2}\sum_{m=1}^{r} I_{qm}(\mu)\int_{-\infty}^{0} e^{\mu t}(y_m^{(+)}(t')+y_m^{(-)}(t'))\,dt', \qquad (A.10)$$

$$g_q(\mu)=\pi d_q(\mu)\operatorname{ctg}\pi\chi(\mu). \qquad (A.11)$$

For each value of μ, the system (A.9) has r solutions. Therefore, it is necessary to consider further the matrix of the solutions $y_{pm}^{(\kappa)}(t)$, as well as the matrices $d_{pm}(\mu)$ and $g_{pm}(\mu)$; Eq. (A.11) also includes the cotangent of the matrix $\hat{\chi}$ and Eq. (A.8) the trace of this matrix. The matrix $\hat{\chi}$ can be found by assuming that $g_{pm}(\mu) = \delta_{pm}$. Then, (A.9) transforms into a system of inhomogeneous integral equations. Having found the matrix of solutions by, for example, the iteration method, we can apply Eq. (A.10) to calculate the matrix $d_{pq}(\mu)$. Since g_{pm} is a unit matrix, the condition (A.11) gives the matrix $\cot(\pi\hat{\chi})$. A reduction of this matrix to the diagonal form gives the trace of the matrix $\hat{\chi}$ and the required integral (A.8).

There are also such values of $\mu = \mu_g$ for which the spectral density $\nu(\mu_g)$ becomes infinite (limiting frequencies) and the system (A.9) does not predict a frequency shift. In addition to a quasicontinuous spectrum of the (A.7) type, we can have—in the limit $N \to \infty$—discrete eigenvalues split off from the limiting points. These eigenvalues should be found directly from the system (A.6). Each such eigenvalue Λ_p makes an additional contribution $F(\Lambda_p) - F(\mu_g)$ to the trace (A.8).

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