

Orbital momentum, Zeeman energy, and spin-orbit interaction in noncentral ions

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(Submitted June 24, 1972)

Zh. Eksp. Teor. Fiz. **64**, 989-992 (March 1973)

It is shown that a nonvanishing orbital angular momentum and a related magnetic moment exist in noncentral ions. The energies of interaction between the magnetic moment and external magnetic field (Zeeman energy) and nuclear magnetic moment (spin-orbit coupling) are estimated. The problem of experimental manifestation of the effects is discussed. A concrete analysis is carried out for an ion tunnelling in an eight-well potential (e.g. Li^+ in KCl).

It has been established (see, for example, [1]) that for certain substitutional impurity ions there exist several equivalent equilibrium positions that do not coincide with crystal-lattice sites. Hence the name "noncentral ions." The ion describes a motion between these positions that leads to tunnel splitting of the levels (analogous to the inversion splitting in the Jahn-Teller effect [2]). The presence of tunnel levels of triply degenerate terms in the system and the clear-cut representation of the spatial motion of the non-central ion point to the possible existence of a nonzero orbital angular momentum of the ion. This assumption is confirmed in the present paper by direct calculations.

1. MATRIX ELEMENTS OF THE ANGULAR MOMENTUM OPERATOR

We consider a case when the impurity ion in a lattice of the NaCl type has eight equivalent equilibrium positions [3,4] displaced in the [111] direction away from the symmetry axis (see the figure). In this case the system of tunnel levels consists of two nondegenerate terms and two triply degenerate terms with an arrangement (in increasing order) $A_{1g}, T_{1u}, T_{2g}, A_{2u}$ [5].

We consider for concreteness the term T_{1u} . Its three orthonormalized functions can be represented in the form

$$\Psi_{1,3} = \pm \frac{A}{\sqrt{2}} (\Psi^{(1)} \mp i\Psi^{(2)}), \quad \Psi_2 = A\Psi^{(3)}, \quad (1)$$

where

$$\Psi^{(1,2,3)} = \varphi_1 \mp \varphi_2 \mp \varphi_3 \pm \varphi_4 \pm \varphi_5 \mp \varphi_6 - \varphi_7 \pm \varphi_8, \quad (2)$$

φ_i is a single-well oscillator function:

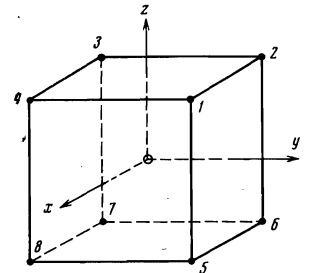
$$\varphi_i = \left(\frac{m\omega}{\pi\hbar} \right)^{3/4} \exp \left\{ -\frac{m\omega}{2\hbar} |\mathbf{r} - \mathbf{R}_i|^2 \right\}, \quad (3)$$

m is the ion mass, ω is the frequency of the oscillations in one of the potential wells, \mathbf{R}_i is the coordinate of the equilibrium position, and A is a normalization factor. The functions $\Psi^{(1)}$, $\Psi^{(2)}$, and $\Psi^{(3)}$ are transformed under the action of the operations of group O_h like the components of the polar vector \mathbf{r} .

Taking into account the transformation properties of the angular-momentum operator \mathbf{l} and using the perturbation-matrix method [6,7], we can find the matrix elements of the components of the operator \mathbf{l} on the functions (1), i.e., represent the operators \hat{l}_k in the matrix form. All the nonzero matrix elements are expressed in terms of a single parameter

$$\beta = \int \Psi_s^* \mathbf{l} \Psi_s d\tau. \quad (4)$$

Equilibrium positions of the ion and the choice of coordinates: \circ —position of cation in an ideal crystal, \bullet —displaced equilibrium position. The coordinate axes are directed along crystallographic axes of the type [100].



Substituting (1)–(3) and the explicit form of the operator \mathbf{l}_z (see, for example, [8]) in (4), we obtain after a number of transformations [2]

$$\beta = \hbar k / \text{sh } k, \quad k = m\omega a^2 / \hbar, \\ a = |R_x| = |R_y| = |R_z|.$$

2. ZEEMAN ENERGY AND SPIN-ORBIT INTERACTION

The interaction energy of the orbital magnetic moment with the external magnetic field can be represented in the form

$$\hat{W}_{\text{Zeem}} = -\frac{e}{2mc} \mathbf{H} \mathbf{l},$$

where e is the ion charge and c is the speed of light. Using the matrices of the operator \mathbf{l} , we obtain energy levels of the term T_{1u} in an external magnetic field:

$$E_{T_{1u}} = E_{T_{1u}}^0 + \Delta_i,$$

$E_{T_{1u}}^0$ is the energy at $H = 0$,

$$\Delta_{1,3} = \pm \mu_0 H, \quad \Delta_2 = 0, \quad \mu_0 = e\beta / 2mc.$$

In accordance with [9], we have for the energy of the spin-orbit interaction

$$W_{c-o} = -\frac{\hbar}{2m^2 c^2} \mathbf{J} [\nabla V \times \mathbf{p}], \quad (5)$$

∇V is the gradient of the potential energy and \mathbf{J} is the spin of the ion.

The operator $\hat{T} = [\nabla V \times \mathbf{p}]$ has the same transformation properties as the operator \mathbf{l} considered above. The matrix form of its components therefore differs only by the parameter

$$\beta' = \int \Psi_s^* \hat{T}_z \Psi_s d\tau. \quad (6)$$

Substituting the expressions for \hat{T}_z in (6), using the explicit form of the functions φ_i , and taking into account the symmetry properties of the operator ∇V , we obtain for the spin-orbit interaction constant λ the equation [3]

$$\lambda = \frac{8a\omega\hbar A^2}{mc^2} \left[\left(\frac{\partial V}{\partial x} \right)_{i,4} + \left(\frac{\partial V}{\partial x} \right)_{i,8} \right],$$

$$\left(\frac{\partial V}{\partial x} \right)_{i,j} = \int \varphi_i \frac{\partial V}{\partial x} \varphi_j d\tau.$$

The expression in the square brackets can be transformed by integrating by parts to a form in which the potential is directly under the integral sign. We calculate the resultant integrals by specifying the following model potential V : we assume that the potential in a cube with side $2b$ ($b \geq a$) is constant ($V = -|V_0|$), and that $V = 0$ everywhere else. The center of the cube is located at a lattice site. As a result of the calculations we get

$$\lambda = \frac{a}{2c^2} \sqrt{\frac{\hbar\omega^3}{\pi m}} |V_0| \frac{\Phi(n\sqrt{2k}) \text{sh}(2kn) \exp[-k(1+n^2)]}{(1+e^{-k}) \text{sh} k}$$

$$\times \{ \Phi[(n-1)\sqrt{2k}] + \Phi[(n+1)\sqrt{2k}] + 2e^{-k} \Phi(n\sqrt{2k}) \},$$

$$n = \frac{b}{a}, \quad \Phi(t) = \sqrt{\frac{2}{\pi}} \int_0^t \exp\left(-\frac{z^2}{2}\right) dz$$

is the probability integral.

3. DISCUSSION OF RESULTS

To estimate the effects we put, in accordance with^[1,4,10], $a = 0.35 \times 10^{-8}$ cm and $\omega = 7.5 \times 10^{12}$ rad/sec. The energy $|V_0|$ is of the order of magnitude of the binding energy of Li^+ in the lattice, so that^[11] $|V_0| = 8.5$ eV. Then, putting $m = 10^{-28}$ g and $n = 1$ we obtain $k = 0.87$, $\mu_0 = 0.15\mu_{\text{nuc}}$, $\lambda = 0.37 \times 10^3$ Hz, and μ_{nuc} is the nuclear magneton. For comparison, we indicate that the magnetic moment of the Li^6 nucleus is $0.82\mu_{\text{nuc}}$.

The spin-orbit interaction can also be estimated by starting from the expression for the energy of interaction between two magnetic moments, in analogy with the procedure used in^[8] for the spin-orbit interaction of an electron. Putting $\mu_1 = 0.15\mu_{\text{nuc}}$ and $\mu_2 = 0.82\mu_{\text{nuc}}$, and choosing $2a$ to be the characteristic distance, we obtain for λ the value 1.3×10^3 Hz, which is 3.5 times larger than the value obtained above. In estimating μ_0 we have assumed that the charge of the lithium ion has the same absolute value as the electron charge. If, however, the idea of total charge transfer in ionic crystal is only approximate^[12], then the chosen value of e is somewhat too high. An experimental determination of μ_0 would yield a more accurate value of e .

In principle, one can propose several experiments for the observation of effects connected with the existence of the orbital angular momentum. The most promising will be apparently experiments in strong external magnetic fields. Since the external field H splits the degenerate terms, one can expect a splitting of the paraelectric resonance line (PER)^[5] analogous to the Zeeman effect in optics. The probability of the transition from the ground term to one of the magnetic sublevels, just as in optics, depends on the orientation of the vector of the electric field that produces the transition. The difficulties in this case are connected with the large width of the PER line. It is therefore necessary to apply strong magnetic fields ($H > 10^4$ Oe), just as strong electric fields ($E \gtrsim 10^5$ V/cm) are some-

times necessary to observe the splitting of lines by an electric field in paramagnetic resonances^[13]. We call attention, however, to the fact that the need for using large magnetic field intensities can be obviated by using pulse techniques^[14]. It is of interest to observe the analog of nuclear magnetic resonance at the excited levels. Since the spin-orbit interaction is small in the systems considered, the ($\mathbf{J} \cdot \mathbf{L}$) coupling in magnetic fields will be broken and two "independent" lines are to be expected in the spectrum. It is possible that the analog of electron-nuclear double resonance^[15], namely the observation of the orientation of the angular momentum \mathbf{l} by means of the PER signal, may be useful here. We note in conclusion that the phenomena considered above can apparently take place in systems in which the Jahn-Teller effect exists.

I am grateful to M. F. Deĭgen for a discussion of the results.

¹⁾The term designation agrees with that in [3-5].

²⁾The use of the transformation properties of the matrix-element components greatly simplifies the derivations.

³⁾We determine the constant λ by comparing (5) with the expression for $\lambda(\mathbf{J} \cdot \mathbf{L})$, where $L = 1/\beta = T/\beta'$.

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Translated by J. G. Adashko

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