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Abstract

Full Text

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A PARAMETRIZATION METHOD FOR PERTURBATION THEORY FOR SYSTEMS WITH SR-SYMMETRY

(Presented by Academician S. V. Vonsovskii on 6 VI 1968)

It is known that perturbation theory for a degenerate level of a quantum system can be formulated in the form of an equivalent Hamiltonian ([1,2]). To calculate the matrix elements of the equivalent Hamiltonian it is necessary to use specific wave functions of the zero approximation. The exact form of these functions is in many cases known only approximately, especially for many-particle systems (molecule, impurity complex, etc.). Meanwhile, in the case of systems possessing a sufficiently high degree of symmetry, all matrix elements of the equivalent Hamiltonian (and consequently all corrections to the eigenvalues of the energy) can be expressed in terms of a certain limited number of parameters. These expressions do not depend on the explicit form of the wave functions of the system and are determined entirely by symmetry properties. A typical example of such a parametrization is the spin-Hamiltonian method ([3]), used in the theory of EPR spectra for an orbitally nondegenerate level.

However, this method is not unconditionally applicable in the case of an orbitally degenerate level, and also in the case when in the zero approximation the system is substantially nonspherical (the angular-momentum operator is not an integral of the motion)*.

There are also semiempirical methods of perturbation theory, for example the method of spin invariants ([4]) in EPR theory or the method of the effective Hamiltonian ([5]) in the theory of optical spectra of impurity ions. However, these methods do not make it possible to calculate the values of the parameters of the theory. To estimate the parameters in these cases one must each time turn to the usual form of perturbation theory.

It is desirable to formulate perturbation theory in such a form that the symmetry of the system is taken into account from the very beginning and, owing to this, the corresponding parameters in the equivalent Hamiltonian are singled out. This can be done by using the algebra of irreducible tensor operators introduced by Racah ([6–8]) for the rotation group and generalized by Wigner ([9]) for arbitrary simply reducible groups (SR-groups)**. The class of SR-groups includes the rotation group and many of the point groups. In the present work we shall restrict ourselves to considering only systems possessing the symmetry of an SR-group.

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Let us consider a quantum system with Hamiltonian

$$\hat{H} = \hat{H}_0 - \varepsilon\hat{V}, \tag{1}$$

for which the zero-approximation Hamiltonian $\hat{H}_0$ is invariant in the simply reducible group G_0; ε is a small perturbation parameter, and the symmetry group of the full Hamiltonian will be denoted by G_H. In contrast to

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* For a weak deviation from spherical symmetry the application of the spin-Hamiltonian method is possible to some extent.

** On SR-groups see, for example, ([9–11]).

[1,2], we use the variant of perturbation theory developed in [12]. According to [12], we first carry out such a unitary transformation $\hat{S}$ of the Hamiltonian $\hat{H}$ that the matrix elements of the new Hamiltonian $\hat{S}^{-1}\hat{H}\hat{S}$, which connect the states of the level under consideration $E_m^{(0)}$ with states of other levels $E_n^{(0)}$, vanish in the second approximation. Neglecting such matrix elements altogether, one can compute corrections to the energy of the level up to order ε^4 [12]. This is sufficient in the overwhelming majority of practical applications. The remaining matrix elements may be represented as matrix elements of the equivalent Hamiltonian:

$$\widetilde{\mathcal{H}}(m) = \hat{H}_0 + \varepsilon\hat{V} + \varepsilon^2 \sum_n \frac{\hat{V}\hat{\mathcal{P}}_n\hat{V}}{E_m^{(0)} - E_n^{(0)}} + \varepsilon^3 \sum_{nn'} \frac{\hat{V}\hat{\mathcal{P}}_n\hat{V}\hat{\mathcal{P}}_{n'}\hat{V}}{\left(E_m^{(0)} - E_n^{(0)}\right)\left(E_m^{(0)} - E_{n'}^{(0)}\right)} - \frac{\varepsilon^3}{2}\sum_n \frac{\hat{V}\hat{\mathcal{P}}_m\hat{V}\hat{\mathcal{P}}_n\hat{V} + \hat{V}\hat{\mathcal{P}}_n\hat{V}\hat{\mathcal{P}}_m\hat{V}}{\left(E_m^{(0)} - E_n^{(0)}\right)^2}, \tag{2}$$

where $\hat{\mathcal{P}}_m$ and $\hat{\mathcal{P}}_n$ are the projection operators [1] onto the spaces of the levels $E_m^{(0)}$ and $E_n^{(0)}$, respectively. Taking into account the symmetry of H_0, we characterize the energy levels by irreducible representations Γ of the group G_0: $E_m^{(0)} \equiv E^{(0)}(\alpha\Gamma)$ and $E_m^{(0)} \equiv E^{(0)}(\alpha_0\Gamma_0)$ (α distinguishes levels of the same type). The projection operator onto the space of the level $E^{(0)}(\alpha\Gamma)$ has the form $\hat{\mathcal{P}}_{\alpha\Gamma} = \sum_\mu \hat{\mathcal{P}}_{\alpha\Gamma\mu}$, where μ "numbers" the rows of Γ. As μ one may choose the so-called projection of the quasimoment [13] onto the principal symmetry axis of the group G_0.

Let the perturbation operator have the form of a linear combination of irreducible tensor operators of the group G_0:

$$\varepsilon\hat{V} = \varepsilon \sum_{\alpha\Gamma\mu} A(\alpha\Gamma\mu)\hat{X}_\mu^{(\alpha\Gamma)}. \tag{3}$$

For brevity of exposition, we restrict ourselves here to the second order of perturbation theory. Substituting (3) into (2) and introducing effective operators:

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$$\hat{Y}_{\mu}^{(\Gamma)}(\alpha_1\Gamma_1;\alpha_2\Gamma_2) = \sum_{\mu_1\mu_2}(\Gamma_1\mu_1;\Gamma_2\mu_2 \mid \Gamma\mu)\left(\hat{X}_{\mu_1}^{(\alpha_1\Gamma_1)}\hat{\mathcal{P}}\hat{X}_{\mu_2}^{(\alpha_2\Gamma_2)} + \hat{X}_{\mu_2}^{(\alpha_2\Gamma_2)}\hat{\mathcal{P}}\hat{X}_{\mu_1}^{(\alpha_1\Gamma_1)}\right), \tag{4}$$

where $(\Gamma_1\mu_1;\Gamma_2\mu_2 \mid \Gamma\mu)$ are the Clebsch–Gordan coefficients of the SR-group G_0 [14], and

$$\hat{\mathcal{P}} = \sum_{\bar{\alpha}\bar{\Gamma}\mu}{}' \hat{\mathcal{P}}_{\bar{\alpha}\bar{\Gamma}\mu} / \left[E^{(0)}(\alpha_0\Gamma_0) - E^{(0)}(\bar{\alpha}\bar{\Gamma})\right] \tag{5}$$

(the prime on the summation sign means $\bar{\alpha}\bar{\Gamma} \neq \alpha_0\Gamma_0$), we obtain

$$\widetilde{\mathcal{H}}(\alpha_0\Gamma_0) = \hat{H}_0 + \varepsilon\sum_{\alpha\Gamma\mu} A(\alpha\Gamma\mu)\hat{X}_{\mu}^{(\alpha\Gamma)} + \varepsilon^2 \sum_{\alpha_1\Gamma_1;\ \alpha_2\Gamma_2;\ \Gamma\mu} B(\alpha_1\Gamma_1;\alpha_2\Gamma_2;\Gamma\mu)\times$$

$$\times\hat{Y}_{\mu\cdot}^{(\Gamma)}(\alpha_1\Gamma_1;\alpha_2\Gamma_2), \tag{6}$$

where

$$B(\alpha_1\Gamma_1;\alpha_2\Gamma_2;\Gamma\mu) = \frac{1}{2}\sum_{\mu_1\mu_2} A(\alpha_1\Gamma_1\mu_1)A(\alpha_2\Gamma_2\mu_2)(\Gamma\mu \mid \Gamma_1\mu_1;\Gamma_2\mu_2). \tag{7}$$

It can be shown that the operator $\hat{\mathcal{P}}$ is invariant with respect to transformations of the group G_0. It follows from this that the effective operators (4) do indeed transform according to the corresponding irreducible representations Γ of the group G_0. From the Hermiticity of the operator (3) it follows that only integer representations [9,11] of the SR-group G_0, for which $(-1)^{2j(\Gamma)} = +1$ ($j(\Gamma)$ is the quasimoment [13,14] of the representa-

of the representation Γ. Hence, in turn, follows the Hermiticity of the operator (6). It is also not difficult to prove that the operator (6) is invariant in the group of transformations G_H.

The types of operators $X^{(\alpha\Gamma)}$ that must be taken into account in (6) are determined by the form of the perturbation and by the condition $\Gamma \in \Gamma_0 \times \Gamma_0$ (operators not satisfying the latter condition have zero matrix elements in the space $E^{(0)}(\alpha_0\Gamma_0)$, as follows from the selection rules).

The number of different types of operators $Y_{\mu}^{(\Gamma)}(\alpha_1\Gamma_1;\alpha_2\Gamma_2)$ is determined by the conditions: 1) $\Gamma \in \Gamma_0 \times \Gamma_0$, 2) $\Gamma \in \Gamma_1 \times \Gamma_2$, 3) $A_1 \in \Gamma$. The last condition means that Γ contains the identity representation A_1 of the group G_H and is the condition for the possibility of constructing from the components $Y_{\mu}^{(\Gamma)}$ an

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invariant in the group G_H. These conditions restrict the number of operators of different type entering the equivalent Hamiltonian.

Since both sums in (6) must be invariant in the group G_H, this means that, for those types of operators $\hat{X}^{(\alpha\Gamma)}$ and $\hat{Y}^{(\Gamma)}$ that actually enter the equivalent Hamiltonian, the coefficients $A(\alpha\Gamma\mu)$ and $B(\varkappa\Gamma\mu)$ must be proportional, i.e.,

$$A(\alpha\Gamma\mu) = a(\alpha\Gamma)C_\mu, \qquad B(\varkappa\Gamma\mu) = b(\varkappa\Gamma)C_\mu, \tag{8}$$

where $\varkappa = \{\alpha_1\Gamma_1; \alpha_2\Gamma_2\}$, and C_μ is determined by the symmetry of the group G_H. Introducing the operators

$$\hat{U}_\mu^{(\Gamma)} = \sum_\alpha a(\alpha\Gamma)X_\mu^{(\alpha\Gamma)} + \sum_\varkappa b(\varkappa\Gamma)Y_\mu^{(\Gamma)}(\varkappa) + \cdots, \tag{9}$$

one may represent the equivalent Hamiltonian in the form

$$\widetilde{\mathcal{H}}(\alpha_0\Gamma_0) = \hat{H}_0 + \sum_{\Gamma\mu} C_\mu \hat{U}_\mu^{(\Gamma)}. \tag{10}$$

The dots in (9) indicate that, when third and higher orders of perturbation theory are taken into account, additional operators will, generally speaking, appear in this expression. Thus, the effective operators $\hat{U}_\mu^{(\Gamma)}$ turn out to be expressed through the operators $\hat{X}, \hat{Y}, ...$, each of which represents a contribution of a definite order of perturbation theory.

In contrast to the semiempirical method (5), in which the true operators $\hat{U}_\mu^{(\Gamma)}$, introduced above in (9), are replaced by certain arbitrary* effective operators $\hat{U}_\mu^{(\Gamma)\,\mathrm{eff}}$ (transforming, however, according to the same representations Γ), in our case explicit expressions are available for the microstructure of these operators, following from perturbation theory.

The possibility of replacing $\hat{U}_\mu^{(\Gamma)} \to \hat{U}_\mu^{(\Gamma)\,\mathrm{eff}}$ for semiempirical calculations is based on the Wigner-Eckart theorem, according to which the matrix elements $\langle\alpha_0\Gamma_0\mu_0|U_\mu^{(\Gamma)}|\alpha_0\Gamma_0\mu_0'\rangle$ and $\langle\alpha_0\Gamma_0\mu_0|\hat{U}_\mu^{(\Gamma)\,\mathrm{eff}}|\alpha_0\Gamma_0\mu_0'\rangle$ are proportional to each other (i.e., their ratio does not depend on μ_0, μ, μ_0'). Applying the Wigner-Eckart theorem, we find

$$\begin{aligned}\langle\alpha_0\Gamma_0\mu_0|\widetilde{\mathcal{H}}(\alpha_0\Gamma_0)|\alpha_0\Gamma_0\mu_0'\rangle &= \delta_{\mu_0\mu_0'}E^{(0)}(\alpha_0\Gamma_0)+\\ &+\sum_{\Gamma\mu} C_\mu(\Gamma_0\mu_0|\Gamma\mu;\Gamma_0\mu_0')\langle\alpha_0\Gamma_0\|U^{(\Gamma)}\|\alpha_0\Gamma_0\rangle.\end{aligned} \tag{11}$$

After solving the secular equation:

$$\mathrm{Det}\left[\langle\alpha_0\Gamma_0\mu_0|\widetilde{\mathcal{H}}(\alpha_0\Gamma_0)|\alpha_0\Gamma_0\mu_0'\rangle - \delta_{\mu_0\mu_0'}E\right] = 0 \tag{12}$$

* The arbitrariness is associated with a particular choice of reduced matrix elements of these operators.

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the eigenvalues of the energy turn out to be expressed in terms of the Clebsch –Gordan coefficients and a rather limited set of parameters $\langle\alpha_0\Gamma_0\|U^{(\Gamma)}\|\alpha_0\Gamma_0\rangle$. The dependence of the eigenvalues of the energy sublevels on these parameters is determined by the symmetry of the problem and the symmetry Γ_0 of the term $E^{(0)}(\alpha_0\Gamma)$ under consideration. The calculation of the parameters themselves requires the use of the explicit wave functions of the system in the zeroth approximation.

According to (9), we have:

$$\langle\alpha_0\Gamma_0\|U^{(\Gamma)}\|\alpha_0\Gamma_0\rangle = \sum_a a(a\Gamma)\langle\alpha_0\Gamma_0\|X^{(a\Gamma)}\|\alpha_0\Gamma_0\rangle+$$

$$+\sum_x b(x\Gamma)\langle\alpha_0\Gamma_0\|Y^{(\Gamma)}(x)\|\alpha_0\Gamma_0\rangle + ... \tag{13}$$

All the matrix elements appearing in (13) can be expressed through the corresponding matrix elements of the operators $\hat{X}^{(a\Gamma)}$. For example, for operators of second order in perturbation theory one can obtain

$$\langle\alpha_0\Gamma_0\|\hat{Y}_\mu^{(\Gamma)}(\alpha_1\Gamma_1;\alpha_2\Gamma_2)\|\alpha_0\Gamma_0\rangle = [\Gamma]^{1/2}\sum_{\overline{a\Gamma}}{}'[\overline{\Gamma}]^{1/2}(-1)^{2j(\Gamma_0)+j(\Gamma)+j(\Gamma_1)+j(\Gamma_2)}\times$$

$$\times\left[(-1)^{j(\Gamma)}\begin{Bmatrix}\Gamma_1\Gamma_2\Gamma\\ \Gamma_0\Gamma_0\overline{\Gamma}\end{Bmatrix}+\begin{Bmatrix}\Gamma_2\Gamma_1\Gamma\\ \Gamma_0\Gamma_0\overline{\Gamma}\end{Bmatrix}\right]\frac{\langle\alpha_0\Gamma_0\|\hat{X}^{(\alpha_1\Gamma_1)}\|\alpha\Gamma\rangle\langle\alpha\overline{\Gamma}\|\hat{X}^{(\alpha_2\Gamma_2)}\|\alpha_0\Gamma_0\rangle}{E^{(0)}(\alpha_0\Gamma_0)-E^{(0)}(\alpha\overline{\Gamma})},$$

where $[\Gamma]$ denotes the dimension of the representation Γ, and

$$\begin{Bmatrix}\Gamma_1\Gamma_2\Gamma_3\\ \Gamma_4\Gamma_5\Gamma_6\end{Bmatrix}$$

is a 6Γ-coefficient of the group G_0 ([15,16]). Tables of such coefficients for point-symmetry groups are available in ([15,16]).

The method considered makes it possible to parametrize the effective Hamiltonian of perturbation theory for a degenerate level of a quantum system (the zeroth-approximation Hamiltonian of which possesses the symmetry of an SR-group) and to calculate the parameters of the effective Hamiltonian.

The application of the method to concrete problems will be given in special papers.

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CITED LITERATURE

1. N. N. Bogolyubov, *Lectures on Quantum Statistics*, Kiev, 1949.
2. M. H. L. Pryce, Proc. Phys. Soc. A, **63**, 25 (1950).
3. A. Abragam, M. H. L. Pryce, Proc. Roy. Soc. A, **205**, 135 (1951).
4. A. M. Leushin, *Collected Works in Paramagnetic Resonance*, Kiev, 1964.
5. Y. Tanabe, H. Kamimura, J. Phys. Soc. Japan, **13**, 394 (1958).
6. G. Racah, Phys. Rev., **62**, 438 (1942).
7. A. P. Yutsis, I. B. Levinson, V. V. Vanagas, *The Mathematical Apparatus of the Theory of Angular Momentum*, Vilnius, 1960.
8. I. I. Sobelman, *Introduction to the Theory of Atomic Spectra*, Moscow, 1963.
9. E. Wigner, *On the Matrices which Reduce the Kronecker Products of Representations of SR-Groups*, Princeton, 1951.
10. D. G. Sviridov, Yu. F. Smirnov, DAN, **163**, 1138 (1965).
11. M. Hamermesh, *Group Theory and Its Application to Physical Problems*, Moscow, 1966.
12. O. M. Jordahl, Phys. Rev., **45**, 87 (1934).
13. M. A. El' yashevich, *Spectra of the Rare Earths*, Moscow, 1953.
14. I. V. Batarunas, I. B. Levinson, Tr. AN LitSSR, ser. B, **2** (22), 15 (1960).
15. E. V. Mauza, I. B. Batarunas, Tr. AN LitSSR, ser. B, **3** (26), 27 (1961).
16. I. S. Griffith, *The Theory of Transition Metal Ions*, Cambridge, 1961.

Note: Figure translations are in progress. See original paper for figures.

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