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Abstract

Full Text

MATHEMATICAL PHYSICS

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**ON THE MATHEMATICAL THEORY OF
ATOMIC SPECTRA**

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The classification of atomic spectra is based on the symmetry properties of the solutions of the equation

$$H\psi = \lambda\psi,$$

where

$$H = H_n = T_n + V_n + W_n; \quad T_n = -a \sum_{i=1}^n \Delta_i, \quad a > 0;$$

$$V_n = -b \sum_{i=1}^n |r_i|^{-1}, \quad b \geq 0; \quad W_n = c \sum_{i \neq j} |r_i - r_j|^{-1}, \quad c \geq 0;$$

$$r_i = (x_i, y_i, z_i), \quad n \geq 2.$$

This equation has three symmetry groups: the permutation group S_n , the rotation group \mathfrak{R}_0 , and the inversion group \mathfrak{B} . If k, l, ω are indices of irreducible representations of these groups, then their direct product

$$\mathfrak{P} = S_n \times \mathfrak{R}_0 \times \mathfrak{B}$$

has irreducible representations with index $\sigma = (k, l, \omega)$, determining the possible types of symmetry of the function ψ . In the literature on the theory of atomic spectra it is stated that, regarding the solutions $\psi^{kl\omega}$, only their symmetry properties are known (see, for example, (1)). Here the question is about the symmetry of solutions whose existence has not been proved. In the present note we give results showing the existence of an infinite sequence of eigenvalues for each type of symmetry $\sigma = (k, l, \omega)$. At the same time, infinite series of eigenvalues of the operator H_n , $n \geq 2$, corresponding to certain symmetry classes σ , are found which lie on the limiting spectrum of the operator H_n of other symmetry classes (Theorem 3)*.

1. The index $\sigma = (\Sigma, l, \omega)$ will denote irreducible representations of the group $\mathfrak{R}_0 \times \mathfrak{B}$, and the index (Σ, l, Σ) irreducible representations of the group \mathfrak{R}_0 , etc. Together with the projection operators $P^{(k)}$, $\overline{P}^{(k)}$, defined by the group S_n (see (2)), we shall also consider the operators

$$P^{\Sigma, l, \Sigma} = (2l + 1) \int_{\mathfrak{R}_0} \chi^l(R) {}^*T_R dR,$$

where $\chi^l(R)$, $R \in \mathfrak{R}_0$, are the characters of the irreducible representation of the group \mathfrak{R}_0 ($l = 0, 1, \dots$), and T_R is the rotation operator (3). The operators $P^{\Sigma, \Sigma, \omega}$, $\omega = \pm 1$, are defined analogously. Put

$$P^\sigma = P^{k, \Sigma, \Sigma} P^{\Sigma, l, \Sigma} P^{\Sigma, \Sigma, \omega}$$

for $\sigma = (k, l, \omega)$. The operators P^σ are projection operators, and

$$P^{\sigma_1} P^{\sigma_2} = P^{\sigma_2} P^{\sigma_1} = 0$$

if $\sigma_1 \neq \sigma_2$. The operators \overline{P}^σ arise when the representation D^k of the group S_n is replaced by the associated representation $\overline{D}^{(k)}$. Let $\mathfrak{H}_n = \mathfrak{H}$ be the Hilbert space of complex-valued functions defined in the entire $3n$ -dimensional Euclidean space

$$R_n = \{x, y, z, \dots, x_n, y_n, z_n\}.$$

Put

$$\mathfrak{H}^\sigma = P^\sigma \mathfrak{H}, \quad \overline{\mathfrak{H}}^\sigma = \overline{P}^\sigma \mathfrak{H}.$$

By the Pauli principle only the spaces $\overline{\mathfrak{H}}^\sigma$ have physical meaning. Since

* If only permutation symmetry is taken into account, this can be proved only for $n \geq 3$ (see (2)).

the exposition for $\overline{\mathfrak{H}}^\sigma$ does not differ essentially from the exposition for \mathfrak{H}^σ ; we shall consider only \mathfrak{H}^σ .

2. By H_n^σ we shall denote the extension of the operator H , considered only on $C_f^2 \cap \mathfrak{H}_n^\sigma$, to a self-adjoint one. Put

$$W_2^1(D_n^\sigma) = \{\psi \in \mathfrak{H}_n^\sigma, \|\text{grad } \psi\| < \infty\};$$

$$L[\psi] = a \|\text{grad } \psi\|^2 + (V_n \psi, \psi) + (W_n \psi, \psi);$$

$$\lambda_0^\sigma = \lambda_0(D_n^\sigma) = \inf L[\psi], \quad \psi \in W_2^1(D_n^\sigma), \quad \|\psi\| = 1.$$

For a given $\sigma = (k, l, \omega)$ define σ_1 by the equalities

$$\mathfrak{H}^{\sigma_1} = \mathfrak{H}^{k, \Sigma, \Sigma\theta} \mathfrak{H}^{k, 0, \omega_l}, \quad \omega_l = (-1)^{l+1} \omega \quad \text{for } l > 0;$$

$$\mathfrak{H}^{\sigma_1} = \mathfrak{H}^{k, \Sigma, \Sigma\theta} \sum_{m=0}^{\infty} \mathfrak{H}^{k, m, \omega_m}, \quad \text{for } l = 0.$$

We define the symmetry type σ_2 by decreasing by one the index k in the definition of σ_1 . Put

$$\mu_{n-1}^\sigma = \min\{\lambda_0(D_{n-1}^{\sigma_1}), \lambda_0(D_{n-1}^{\sigma_2})\}.$$

Where the terms depending on k lose their meaning because of violation of the inequalities $0 \leq k \leq [n/2]$, we shall regard these terms as absent.

Theorem 1.

- 1) The inequality $\lambda_0(D_n^\sigma) \leq \mu_{n-1}^\sigma$ always holds.
- 2) In order that $\lambda_0(D_n^\sigma)$ be a point of the discrete spectrum of the operator H_n^σ , it is necessary and sufficient that the condition $\lambda_0(D_n^\sigma) < \mu_{n-1}^\sigma$ be satisfied.
- 3) The points $\lambda \geq \mu_{n-1}^\sigma$ form the limit spectrum of the operator H_n^σ .

3. Theorem 2. Let

$$\lambda_0^\sigma \leq \lambda_1^\sigma \leq \dots \leq \lambda_{p-1}^\sigma \quad (p \geq 1)$$

be eigenvalues; u_0, u_1, \dots, u_{p-1} the corresponding orthonormal eigenfunctions of the operator H_n ,

$$Q_p = \{\psi \in W_2^1(D_n^\sigma), \|\psi\| = 1, (\psi, u_s) = 0; s = 0, 1, \dots, p-1\},$$

$$\lambda_p^\sigma = \lambda_p(D_n^\sigma) = \inf L[\psi], \quad \psi \in Q_p \quad (p \geq 1).$$

- 1) The inequality $\lambda_p(D_n^\sigma) \leq \mu_{n-1}^\sigma$ always holds.
- 2) In order that $\lambda_p(D_n^\sigma)$ be a point of the discrete spectrum of the operator H_n^σ , it is necessary and sufficient that the condition $\lambda_p(D_n^\sigma) < \mu_{n-1}^\sigma$ be satisfied.
4. **Theorem 3.** Suppose the quantities b, c in the expression H_n satisfy the condition $b > (n-1)c$. Then:
 - 1) For $n \geq 2$ and any symmetry type $\sigma = (k, l, \omega)$, except for the type $\sigma = (\Sigma, 0, -1)$ which does not exist for $n = 2$, there exists an infinite sequence of points of the discrete spectrum λ_p^σ ($p = 0, 1, \dots$) of the operator H_n^σ , accumulating at the value μ_{n-1}^σ .

- 2) $\lambda_0^{0,0,+1} < \lambda_0^\sigma$ for $\sigma \neq (0, 0, +1)$.
- 3) For $n = 2$ and $\sigma = (k, l, (-1)^{l+1})$, where k and $l > 0$ are arbitrary fixed indices, all eigenvalues $\{\lambda_p^\sigma\}$ ($p = 0, 1, \dots$), with the exception, perhaps, of a finite number of them, lie on the limit spectrum of the operator $H_2^{\sigma'}$ for any $\sigma' = \{k_1, m, (-1)^m\}$, where k_1, m are arbitrary indices.

Corollary. By virtue of 1)–2), for $n \geq 3$, for each $\sigma = (k, l, \omega)$, $k \geq 2$, all eigenvalues λ_p^σ , except possibly a finite number of them, lie on the limit spectrum of the operator $H_n^{0,0,1}$.

Remark. If $H_2(\varepsilon) = T_2 + V_2 + \varepsilon W_2$, then for $\varepsilon = 0$ the symmetry type $\sigma' = (k, m, (-1)^m)$ is possessed by all eigenfunctions obtained by symmetrization ($k = 0$) or antisymmetrization ($k = 1$) from functions of the form $\psi_0(r_1) \cdot \psi_p(r_2)$, where $\psi_p(r)$ are eigenfunctions of the operator

for H_1 , ψ_0 corresponds to the smallest eigenvalue. However, the eigenfunctions of the operator $H_2(0)$ possessing symmetry σ' are not exhausted by this series. For $H_2(1)$ an analogous fact cannot be established*, since the methods employed yield, for each type of symmetry, only the very lowest series of corresponding eigenvalues.

5. The proof of Theorems 1 and 2 is based on the following proposition.

Theorem 4. Let $\sigma = (k, l, \omega)$ be arbitrary. If $\{\psi_m\} \in C_f^2 \cap \bigcap \mathfrak{L}_n^\sigma u$

$$1) \int_{R_n} |\psi_m|^2 d\Omega + \int_{R_n} |\text{grad } \psi_m|^2 d\Omega \leq c \quad (m = 1, 2, \dots);$$

$$2) \int_{\Omega} |\psi_m|^2 d\Omega \rightarrow 0 \quad (m \rightarrow \infty) \quad \text{for every bounded domain } \Omega \subset R_n,$$

then

$$\lim_{n \rightarrow \infty} L_n[\psi_m] \geq \mu_{n-1}^\sigma.$$

The proofs of these theorems are carried out analogously to (1).

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* Although it apparently does hold.

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

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