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Abstract

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MATHEMATICS

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ON THE EXISTENCE OF EIGENFUNCTIONS FOR THE SCHRÖDINGER EQUATION

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In the present note we consider the question of the existence of eigenfunctions of the Schrödinger equation

$$H\psi = E\psi, \qquad H\psi = -\sum_{i=1}^{n} a_i \Delta_i \psi - \sum_{i=1}^{n} b_i \frac{\psi}{r_i} + \sum_{i<j}^{1,n} c_{ij} \frac{\psi}{r_{ij}}. \tag{1}$$

Here $\psi = \psi(P)$ is the wave function of the system, defined in the whole Euclidean space R_{3n} of the variables $x_i, y_i, z_i,\ i = 1, 2, \dots, n$; $P(x_1 \dots x_n, y_1 \dots y_n, z_1 \dots z_n)$ is an arbitrary point of R_{3n}; E is the value of the energy of the system in the state ψ; $\Delta_i = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$; $r_i = \sqrt{x_i^2 + y_i^2 + z_i^2}$; $r_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}$; a_i, b_i, c_{ij} are positive numbers, $1 \le i < j \le n$; equation (1) is considered in the whole space R_{3n}.

For $n = 1$ the eigenfunctions and eigenvalues of equation (1) are known ([1]). For $n = 2$, for particular values of the coefficients corresponding to the helium atom*, the existence of a countable sequence of eigenvalues of equation (1) was proved by Kato ([2]). For $n > 2$ the question of the existence of eigenvalues of equation (1) had not been studied.

Below a proof is given of the existence of a countable sequence of eigenvalues for systems of general form defined by equation (1)**.

Main theorem. *Let the coefficients b_i and c_{ij} of equation (1) satisfy the inequalities*

$$b_i > \sum_{j \ne i}^{1,n} c_{ij}, \qquad i = 1, 2, \dots, n. \tag{2}$$

Then there exists an infinite sequence of eigenvalues of equation (1); the multiplicity of each of them is finite; the eigenfunctions are differentiable any number of times and satisfy equation (1) at every point lying on none of the manifolds $r_i = 0,\ i = 1, 2, \ldots, n;\ r_{ij} = 0,\ 1 \le i < j \le n.$

1. For the proof of this theorem it is sufficient to consider only real functions. Let $\psi(P)$ and $\varphi(P)$ be measurable functions in R_{3n}. Introduce the following notation:

$$(\psi, \varphi) = \int_{R_{3n}} \psi\varphi \, d\Omega, \qquad \|\psi\|^2 = (\psi, \psi), \qquad \mathcal{L}^2(R_{3n}) = \{\psi(P),\ \|\psi\| < +\infty\}.$$

* $a_1 = a_2 = \hbar^2 \cdot 2m^{-1},\ b_1 = b_2 = 2e^2,\ c_{12} = e^2$, where e and m are the charge and mass of the electron, $\hbar$ is Planck' s constant divided by 2π.

** In particular, the systems considered include all atoms and ions, if one assumes that their nuclei are fixed.

We shall say that a function ψ belongs to the space $W_2^1(R_{3n})$ if ψ has, in every bounded domain of the space R_{3n}, generalized (in the sense of S. L. Sobolev ([3])) derivatives of the first order and the condition

$$\|\psi\|_{W_2^1(R_{3n})} = \int_{R_{3n}} (|\psi|^2 + |\operatorname{grad}\psi|^2) \, d\Omega < +\infty$$

is satisfied.

Let the operator H be defined on D_H (D_H is the collection of all finite twice continuously differentiable functions in R_{3n}) and let the operator $\widetilde{H}$ be a self-adjoint extension of the operator H. Put

$$L[\psi] = (H\psi, \psi) = \sum_{i=1}^{n} a_i \int_{R_{3n}} |\operatorname{grad}_i \psi|^2 \, d\Omega - \sum_{i=1}^{n} b_i \int_{R_{3n}} \frac{|\psi|^2}{r_i} \, d\Omega + \sum_{i<j}^{1,n} c_{ij} \int_{R_{3n}} \frac{|\psi|^2}{r_{ij}} \, d\Omega,$$

where

$$|\operatorname{grad}_i \psi|^2 = \left(\frac{\partial\psi}{\partial x_i}\right)^2 + \left(\frac{\partial\psi}{\partial y_i}\right)^2 + \left(\frac{\partial\psi}{\partial z_i}\right)^2.$$

Define the classes of functions $Q_{3n}^{(p)}$

$$Q_{3n}^{(0)} = \{\psi,\ \psi \in W_2^1(R_{3n}),\ \|\psi\| = 1\};$$

$$Q_{3n}^{(p)}\{\psi,\ \psi \in Q_{3n}^{(0)},\ (\psi,\varphi_l)=0,\ l=0,1,\ldots,p-1\} \quad (p=1,2,\ldots),$$

where φ_l is the function realizing the minimum of the functional $L[\psi]$ in $Q_{3n}^{(l)}$.

Lemma 1. *If there exists a function φ_0 realizing the minimum of the functional $L[\psi]$ in the class $Q_{3n}^{(0)}$, and $\lambda_{3n}^{(0)} = L[\varphi_0]$, then $\lambda_{3n}^{(0)}$ is the smallest eigenvalue of the operator $\widetilde{H}$, and $\widetilde{H}\varphi_0 = \lambda_{3n}^{(0)}\varphi_0$. Suppose there exist functions φ_l such that $L[\varphi_l] = \inf L[\psi]$, $\psi \in Q_{3n}^{(l)}$, $l=0,1,\ldots,p-1$, where p is any fixed natural number. If there exists a function φ_p realizing $\inf L[\psi]$, $\psi \in Q_{3n}^{(p)}$, and $\lambda_{3n}^{(p)} = L[\varphi_p]$, then $\lambda_{3n}^{(p)}$ is the $(p+1)$-st (counting multiplicity) eigenvalue of the operator $\widetilde{H}$, and $\widetilde{H}\varphi_p = \lambda_{3n}^{(p)}\varphi_p$. All numbers λ, $\lambda < \sup \lambda_{3n}^{(p)}$, not coinciding with $\lambda_{3n}^{(p)}$ for any p, are regular points of the operator $\widetilde{H}$.*

This lemma expresses the known extremal properties of eigenvalues ([4]) as applied to the operator $\widetilde{H}$.

2. A sequence of functions $\{u_m\}$ from $\mathcal{L}^2(R_{3n})$ is called **non-escaping** if, for every $\varepsilon > 0$, one can specify a number $A > 0$ such that, for all m and for the chosen A, one has

$$\int_{r>A} |u_m|^2 \, d\Omega < \varepsilon.$$

A sequence $\{u_m\}$ from $\mathcal{L}^2(R_{3n})$ that does not possess this property is called **escaping**.

Lemma 2*. *For the existence of a function realizing $\inf L[\psi]$, $\psi \in Q_{3n}^{(p)}$ $(p \geq 0)$, it is necessary and sufficient that, for the variational problem under consideration, there exist a non-escaping minimizing sequence.*

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* This proposition was first obtained in a work of E. F. Zhizhenkova, carried out at Gorky State University in 1954. See also ([5]).

Proof. The necessity is obvious. The sufficiency is proved by choosing a minimizing sequence that converges weakly in $W_2^1(R_{3n})$ and does not spread, and by using the lower semicontinuity of the functional $L[\psi]$ along this sequence ([6]).

3. A sequence of functions $\{u_m\}$ from $\mathcal{L}^2(R_{3n})$ is called **semispreading** if, for every bounded domain Ω of the space R_{3n}, one has

$$\lim_{m\to\infty} \int_{\Omega} |u_m|^2 \, d\Omega = 0.$$

Lemma 3. If there exists a spreading minimizing sequence $\{\psi_m\}$ for the functional $L[\psi]$ in $Q_{3n}^{(p)}$, then there also exists a completely spreading minimizing sequence for $L[\psi]$ in $Q_{3n}^{(p)}$.

Proof. We may assume that $\{\psi_m\}$ converges weakly in $W_2^1(R_{3n})$ to some function φ_0 from $W_2^1(R_{3n})$. The sequence $v_m = u_m\|u_m\|^{-1}$, $u_m = \psi_m - \varphi_0$, $m = 1, 2, ...$, is minimizing for $L[\psi]$ in $Q_{3n}^{(p)}$. Using Kondrashov' s theorem ([3]) and the fact that the sequence $\{\psi_m\}$ spreads, one can show that $\{v_m\}$ spreads completely.

4. Let $R_{3n-3,i}$ be the $3(n-1)$-dimensional Euclidean space of the variables x_j, y_j, z_j, $j = 1, 2, \dots, i-1, i+1, \dots, n$, $n > 2$; let $P_{3n-3,i}$ be an arbitrary point of the space $R_{3n-3,i}$; and let φ be an arbitrary function from $W_2^1(R_{3n-3,i})$ (the space $W_2^1(R_{3n-3,i})$ is defined analogously to $W_2^1(R_{3n})$).

Set

$$L_{3n-3,i}[\varphi] = \sum_{j\neq i}^{1,n} a_j \int_{R_{3n-3,i}} |\operatorname{grad}_j \varphi|^2 \, d\Omega - \sum_{j\neq i}^{1,n} b_j \int_{R_{3n-3,i}} \frac{|\varphi|^2}{r_j} \, d\Omega + \sum_{\substack{l<j \\ l\neq i,\ j\neq i}}^{1,n} c_{lj} \int_{R_{3n-3,i}} \frac{|\psi|^2}{r_{lj}} \, d\Omega,$$

$$Q_{3n-3,i} = \{\varphi,\ \varphi \in W_2^1(R_{3n-3,i}),\ \|\varphi\| = 1\};$$

$$\lambda_{3n-3,1} = \inf L_{3n-3,i}[\varphi], \quad \varphi \in Q_{3n-3,i}; \qquad \lambda_{0,1} = 0.$$

Lemma 4. Let a completely spreading sequence of functions $\{u_m\}$ satisfy the condition

$$\int_{R_{3n}} |\operatorname{grad} u_m|^2 \, d\Omega < M \qquad (M \text{ does not depend on } m)$$

and $\|u_m\| = 1, \quad m = 1, 2, \dots.$ Then

$$\lim_{m\to\infty} L[u_m] \geq \min_{1\leq i\leq n} \{\lambda_{3n-3,i}\}. \tag{3}$$

If, moreover, it is assumed that $\{u_m\}$ is a minimizing sequence for one of the variational problems of Lemma 1, then the inequality (3) becomes an equality.

The assertion of Lemma 4 (taking Lemma 3 into account) has the following physical meaning: from the existence of a spreading minimizing sequence it follows that the escape of a particle is, on average, energetically favorable or energetically indifferent. In the proof, the change in the mean value of the energy when each of the particles escapes is estimated, and the mean value of the energy of the remaining system is compared with the mean value of the energy of the original system.

II. 5. Theorem. If the numbers b_i and c_{ij} $(1 \le i < j \le n)$ satisfy inequality (2), then there exists a function φ_p realizing $\inf \psi[\psi]$, $L \in Q_{3n}^{(p)}$, $p = 0, 1, 2, \ldots$.

We shall carry out the proof for $p = 0$. By Lemmas 2 and 3 it is enough to show that a minimizing sequence $\{\psi_m\}$ for the functional $L[\psi]$ in the class $Q_{3n}^{(0)}$ cannot disperse completely.

By Lemma 4, for this it is enough to establish that

$$\lambda_{3n}^{(0)} < \lambda_{3n-3,i_0}, \tag{4}$$

where

$$\lambda_{3n}^{(0)} = \lim_{m\to\infty} L[\psi_m], \qquad \lambda_{3n-3,i_0} = \min_{1\le i\le n} \lambda_{3n-3,i}.$$

For $n = 1$ this is obvious, since $\lambda_3^{(0)} < 0$. Suppose inequality (4) holds for $n \le s-1$. We shall prove that (4) is true for $n = s$. Let

$$\lambda_{3s-3,i_0} = \min_{1\le i\le s} \lambda_{3s-3,i};$$

from the induction hypothesis there follows the existence of a function $f(P_{3s-3,i_0})$, $f \in Q_{3s-3,i_0}$, for which

$$L_{3s-3,i_0}[f] = \lambda_{3s-3,i_0}.$$

Let $R^{(i_0)}$ be the 3-dimensional Euclidean space of the variables $x_{i_0}, y_{i_0}, z_{i_0}$; let $g(x_{i_0}, y_{i_0}, z_{i_0})$ be a finite, continuously differentiable function in $R^{(i_0)}$ such that

$$\int_{R^{(i_0)}} |g|^2\, d\Omega = 1.$$

Set

$$\Phi_k = k^{3/2} g(kx_{i_0}, ky_{i_0}, kz_{i_0}) \cdot f(P_{3s-3,i_0}),$$

where k is an arbitrary positive number. It is easy to see that

$$L_s[\Phi_k] = \lambda_{3s-3,i_0} + k^2 a_{i_0} \int_{R_{3s}} |\operatorname{grad}_{i_0} \Phi_1|^2\, d\Omega + k \sum_{\substack{j=1,\ldots,n\\ j\ne i_0}} c_{i_0 j}\{I_j(k) - I_j(0)\} - k\alpha I_j(0),$$

where

$$I_j(k) = \int_{R_{3s}} \frac{|\Phi_1|^2 \, d\Omega}{\sqrt{(x_{i_0} - kx_j)^2 + (y_{i_0} - ky_j)^2 + (z_{i_0} - kz_j)^2}}, \qquad \alpha = b_{i_0} - \sum_{\substack{j=1,\dots,s \\ j \neq i_0}} c_{i_0 j} > 0.$$

$$(I_j(k) - I_j(0)) \to 0 \quad \text{as } k \to 0,$$

and therefore

$$L_{3s}[\Phi_k] < \lambda_{3s-3,i_0}$$

for sufficiently small k. Since $\Phi_k \in Q_{3s}^{(0)}$, it follows from (5) that

$$\lambda_{3s}^{(0)} < \lambda_{3s-3,i_0},$$

which proves the theorem.

The main theorem follows from the theorem just proved, Lemma 1, and Friedrichs' results (7).

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