First-order perturbative solution to Schrödinger equation for charged particles

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Abstract

Perturbative solution to Schrödinger equation for $N$ charged particles is studied. We use an expansion that is equivalent to Fock's one. In the case that the zeroth-order approximation is a harmonic homogeneous polynomial a first-order approximation is found.

1 Introduction

The Schrödinger equation for the purely spatial wave function of $N$ charged particles can be written in the form

$$H\psi(r_1, r_2, \ldots, r_N) = E\psi(r_1, r_2, \ldots, r_N),$$

(1)

$$H = -\frac{1}{2}\Delta + V(r_1, r_2, \ldots, r_N).$$

(2)

Here $r_i = (x_{i1}, x_{i2}, x_{i3})$ is the three-dimensional position vector of the $i$-th particle in cartesian coordinates, $\Delta$ is the Laplace operator in the configuration space of $3N$ variables, $V$ is the Coulomb potential,

$$V = \sum_{i=1}^{N} \frac{q_i}{r_i} + \sum_{i<j=1}^{N} \frac{q_{ij}}{r_{ij}},$$

(3)

$r_i = |r_i|$, $r_{ij} = |r_i - r_j|$, $q_i$ and $q_{ij}$ are constants.
In order to find a perturbative solution to eq. (1) we use an expansion that in hyperspherical coordinates [1] is equivalent to Fock’s one [2]. Let $S$ denote the set of functions of the form

$$f \ln^m h$$

(4)

where $f$ and $h$ are homogeneous functions of $(x_{1\alpha_1}, x_{2\alpha_2}, \ldots, x_{N\alpha_N})$, $\alpha_i = 1, 2, 3, i = 1, 2, \ldots, N, h > 0, m = 0, 1, \ldots$. Function (4) in hyperspherical coordinates can be written in the form of Fock’s expansion

$$f \ln^m h = r^k \sum_{p=0}^{m} a_p (\ln r)^p.$$  

(5)

Here $r = \sqrt{r_1^2 + r_2^2 + \cdots + r_N^2}$, $k = \deg f$, $a_p$ are certain functions of the spherical angles, and the subscript $p$ takes on integer values.

The degree $n$ is prescribed for the function (5) if $f$ is homogeneous of degree $n$,

$$\deg (f \ln^m h) = n.$$  

The set $S$ splits as

$$S = \bigcup_n S_n$$

with $\deg X = n$ for $X \in S_n$. Let $\mathcal{V}_n$ be the span of $S_n$. For any $X \in \mathcal{V}_n$ we define

$$\deg X = n.$$  

This means that for arbitrary homogeneous functions $f_1, f_2, \ldots, f_k$ of degree $n$

$$\deg (f_1 \ln^{m_1} h_1 + f_2 \ln^{m_2} h_2 + \cdots + f_k \ln^{m_k} h_k) = n.$$  

We shall use the following expansion for $\psi$ :

$$\psi = \sum_{n=0}^{\infty} \psi_n,$$  

(6)

where $\psi_0 \in \mathcal{V}_k$, $k \geq 0$, $\psi_n \in \mathcal{V}_{n+k}$. Expansion (6) in hyperspherical coordinates can be also written in the form of Fock’s expansion.

Substituting (6) in (1) one obtains the following equations

$$\Delta \psi_0 = 0,$$  

(7)

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\[ \Delta \psi_1 = 2V\psi_0, \quad (8) \]

\[ \Delta \psi_n = 2V\psi_{n-1} - 2E\psi_{n-2}, \quad (9) \]

\( n = 2, 3, \ldots \). In the case of two-electron atoms these equations were studied by many authors (see e.g. [3] and references therein).

2 General solution to equation for \( \psi_1 \)

Our aim is to find a solution to (8) in the case that \( \psi_0 = p_k \) is a homogeneous polynomial of degree \( k \),

\[ \Delta \psi_1 = 2Vp_k. \quad (10) \]

**Lemma** If \( g \) is a harmonic function and \( p_k \) is a polynomial of degree \( k \) then

\[ \Delta^{k+1}(gp_k) = 0. \quad (11) \]

**Proof** The proof will be by induction on the degree \( k \). For \( k = 0 \) the lemma is true. Suppose the lemma is true for \( k = 0, 1, \ldots, r - 1 \). We have

\[ \Delta^{r+1}(gp_r) = \Delta^r \left( g\Delta p_r + 2 \sum_{i=1}^{N} \sum_{\alpha=1}^{3} \frac{\partial g}{\partial x_{ia}} \frac{\partial p_r}{\partial x_{ia}} \right). \quad (12) \]

Functions \( \Delta p_r, \partial p_r/\partial x_{ia} \) are polynomials of degree \( r - 2 \) and \( r - 1 \) respectively, and \( \partial g/\partial x_{ia} \) is a harmonic function. Hence, by the induction hypothesis, the rhs of (12) is zero. This completes the induction. \( \square \)

**Theorem** General solution to (10) is given by

\[ \psi_1 = \tilde{\psi}_1 + h, \]

where

\[ \tilde{\psi}_1 = \sum_{n=1}^{k+1} \frac{(-1)^{n+1}r^{2n}\Delta^{n-1}(2Vp_k)}{2^n n! (3N + 2k - 2)(3N + 2k - 4) \cdots (3N + 2k - 2n)}. \quad (13) \]

\( h \in V_{k+1}, \Delta h = 0. \)
PROOF We shall seek the solution to eq. (10) in the form
\[
\psi_1 = \sum_{n=1}^{k+1} a_n r^{2n} \Delta^{n-1}(2Vp_k).
\] (14)

It may be verified that if \( f \) is a homogeneous function of degree \( k - 1 \) then
\[
\Delta(r^{2n} \Delta^{n-1} f) = 2n(3N + 2k - 2n)r^{2n-2} \Delta^{n-1} f + r^{2n} \Delta^n f.
\] (15)

Substituting (14) in (10), and using relation (15) we find
\[
a_n = \frac{(-1)^{n+1}}{2^n n! (3N + 2k - 2)(3N + 2k - 6) \ldots (3N + 2k - 2n)},
\] (16)

and hence a particular solution to (10) is given by (13).

Unfortunately function \( \tilde{\psi}_1 \) is discontinuous at \( r_i = 0, r_{ij} = 0 \). In order to get a continuous \( \psi_1 \) we must find a suitable \( h \).

As an example, consider the case \( \psi_0 = 1 \). Eq. (10) takes the form
\[
\Delta \psi_1 = \sum_{i=1}^{N} \frac{2q_i}{r_i} + \sum_{i<j}^{N} \frac{2q_{ij}}{r_{ij}}.
\] (17)

By using (13) we find
\[
\tilde{\psi}_1 = \frac{r^2}{(3N - 2)} \left( \sum_{i=1}^{N} \frac{q_i}{r_i} + \sum_{i<j}^{N} \frac{q_{ij}}{r_{ij}} \right).
\] (18)

A continuous \( \psi_1 \) can be constructed by using the following harmonic functions
\[
h_i = r_i - \frac{r^2}{(3N - 2)r_i}, \quad h_{ij} = r_{ij} - \frac{2r^2}{(3N - 2)r_{ij}}.
\] (19)

\).

We have
\[
\psi_1 = \tilde{\psi}_1 + \sum_{i=1}^{N} h_i + \frac{1}{2} \sum_{i<j=1}^{N} h_{ij} = \sum_{i=1}^{N} q_ir_i + \frac{1}{2} \sum_{i<j=1}^{N} q_{ij}r_{ij}.
\] (20)

Some other examples of constructing continuous \( \psi_1 \) in the case of \( N = 2 \) can be found in [4].
References


