# 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

$$H\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = E\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N), \tag{1}$$

$$H = -\frac{1}{2}\Delta + V(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N). \tag{2}$$

Here $\mathbf{r}_i = (x_{i1}, x_{i2}, x_{i3})$ 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,

$$V = \sum_{i=1}^{N} \frac{q_i}{r_i} + \sum_{i<j=1}^{N} \frac{q_{ij}}{r_{ij}}, \tag{3}$$

$r_i = |\mathbf{r}_i|$, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, $q_i$ 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

$$f \ln^m h \tag{4}$$

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

$$f \ln^m h = r^k \sum_{p=0}^{m} a_p (\ln r)^p. \tag{5}$$

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 expasion for $\psi$ :

$$\psi = \sum_{n=0}^{\infty} \psi_n, \tag{6}$$

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

$$\Delta \psi_0 = 0, \tag{7}$$

$$\Delta\psi_1 = 2V\psi_0, \tag{8}$$

$$\Delta\psi_n = 2V\psi_{n-1} - 2E\psi_{n-2}, \tag{9}$$

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

$$\Delta\psi_1 = 2Vp_k. \tag{10}$$

LEMMA If $g$ is a harmonic function and $p_k$ is a polynomial of degree $k$ then

$$\Delta^{k+1}(gp_k) = 0. \tag{11}$$

PROOF The proof will be by induction on the degree $k$. For $k = 0$ the lemma is true. Suppose the lemma is true for $k = 0, 1, ..., r-1$. We have

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

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

THEOREM General solution to (10) is given by

$$\psi_1 = \widetilde{\psi}_1 + h,$$

where

$$\widetilde{\psi}_1 = \sum_{n=1}^{k+1}\frac{(-1)^{n+1}r^{2n}\Delta^{n-1}(2Vp_k)}{2^n n!\,(3N+2k-2)(3N+2k-4)\ldots(3N+2k-2n)}, \tag{13}$$

$h \in \mathcal{V}_{k+1}$, $\Delta h = 0$.

PROOF We shall seek the solution to eq. (10) in the form

$$\psi_1 = \sum_{n=1}^{k+1} a_n r^{2n} \Delta^{n-1}(2Vp_k). \tag{14}$$

It may be verified that if $f$ is a homogeneous function of degree $k-1$ then

$$\Delta(r^{2n}\Delta^{n-1}f) = 2n(3N+2k-2n)r^{2n-2}\Delta^{n-1}f + r^{2n}\Delta^n f. \tag{15}$$

Substituting (14) in (10), and using relation (15) we find

$$a_n = \frac{(-1)^{n+1}}{2^n n!\,(3N+2k-2)(3N+2k-6)\ldots(3N+2k-2n)}, \tag{16}$$

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

Unfortunately function $\widetilde{\psi}_1$ is discontinuous at $r_i = 0$, $r_{ij} = 0$. 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

$$\Delta\psi_1 = \sum_{i=1}^{N} \frac{2q_i}{r_i} + \sum_{i<j=1}^{N} \frac{2q_{ij}}{r_{ij}}. \tag{17}$$

By using (13) we find

$$\widetilde{\psi}_1 = \frac{r^2}{(3N-2)} \left( \sum_{i=1}^{N} \frac{q_i}{r_i} + \sum_{i<j=1}^{N} \frac{q_{ij}}{r_{ij}} \right). \tag{18}$$

A continuous $\psi_1$ can be constructed by using the following harmonic functions

$$h_i = r_i - \frac{r^2}{(3N-2)r_i}, \qquad h_{ij} = r_{ij} - \frac{2r^2}{(3N-2)r_{ij}}. \tag{19}$$

. We have

$$\psi_1 = \widetilde{\psi}_1 + \sum_{i=1}^{N} h_i + \frac{1}{2}\sum_{i<j=1}^{N} h_{ij} = \sum_{i=1}^{N} q_i r_i + \frac{1}{2}\sum_{i<j=1}^{N} q_{ij} r_{ij}. \tag{20}$$

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

## References


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