An Exploratory Method for Solving
the Stationary Schrödinger Equation

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Abstract
In this paper, we propose a new numerical method for obtaining the
ground state solution of the stationary Schrödinger equation by using
the Monte Carlo integration.

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1 Introduction

Let $H$ be the Hamiltonian for $N$ electrons with position vectors $\{ r_i \}$ and $M$
nuclei with position vectors $\{ R_A \}$ and atomic numbers $\{ Z_A \}$:

$$
-H = \sum_{i=1}^{N} \frac{\nabla_i^2}{2} - \sum_{1 \leq i \leq N} \left( \sum_{1 \leq A \leq M} \frac{Z_A}{|r_i - R_A|} \right) + \sum_{1 \leq i < j \leq N} \frac{1}{|r_i - r_j|}.
$$

For simplicity, we deal with the closed-shell Slater determinant

$$
\Psi = |\psi_1 \alpha \psi_1 \beta \cdots \psi_{N/2} \alpha \psi_{N/2} \beta|,
$$

where $\alpha, \beta$ are spin functions. The electronic energy of this system is

$$
\langle \Psi | H | \Psi \rangle = 2 \sum_{i=1}^{N} \int \psi_i^*(r) \left( -\frac{1}{2} \nabla^2 - \sum_{1 \leq A \leq M} \frac{Z_A}{r_i A} \right) \psi_i(r) dr
$$
\[
+2 \sum_{1 \leq i, j \leq N} \int \int \psi_i^*(r) \psi_i(r) \frac{1}{|r' - r|} \psi_j^*(r') \psi_j(r') dr dr' \\
- \sum_{1 \leq i, j \leq N} \int \int \psi_i^*(r) \psi_j(r) \frac{1}{|r' - r|} \psi_j^*(r') \psi_i(r') dr dr'
\]

(e.g., [3]). We further put

\[
\psi_i = \sum_{k=1}^{n_i} c_{ik} (x - x_{0A_i})^{s_{ik}} (y - y_{0A_i})^{t_{ik}} (z - z_{0A_i})^{u_{ik}} \exp(-\alpha_{ik} |r - R_{A_i}|^2),
\]

where \( r = (x, y, z) \) and \( R_{A_i} = (x_{0A_i}, y_{0A_i}, z_{0A_i}) \). Then it follows that \( \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle \) is the rational function of

\[
c_{ik}, \alpha_{ik}^{1/4}, \sqrt{\alpha_{i_1 k_1} + \alpha_{i_2 k_2}}, \sqrt{\frac{1}{\alpha_{i_1 k_1} + \alpha_{i_2 k_2}} + \frac{1}{\alpha_{i_3 k_3} + \alpha_{i_4 k_4}}},
\]

and the functions of the forms

\[
\exp\left(-\frac{b\alpha_{i_1 k_1} \alpha_{i_2 k_2}}{\alpha_{i_1 k_1} + \alpha_{i_2 k_2}}\right), \int_0^1 u^{2\nu} \exp(-b(\alpha_{i_1 k_1} + \alpha_{i_2 k_2}) u^2) du,
\]

\[
\int_0^1 u^{2\nu} \exp\left(-\frac{b u^2}{1/(\alpha_{i_1 k_1} + \alpha_{i_2 k_2}) + 1/(\alpha_{i_3 k_3} + \alpha_{i_4 k_4})}\right) du
\]

(e.g., [1]). The aim of this paper is to propose a new method for evaluating \( \{c_{ik}, \alpha_{ik}\} \) that minimize \( \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle \).

2 Preliminaries

We write \( \{p_1, \ldots, p_m\} = \{c_{ik}\} \cup \{\alpha_{ik}\} \) and \( \omega(p_1, \ldots, p_m) = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle \). It is easily seen that \( \omega(p_1, \ldots, p_m) \) has the following properties.

**Remark 2.1** Let \( P \) be an \( m \)-dimensional rectangle, let \( S_1 \) be the set of points at which \( \omega(p_1, \ldots, p_m) \) is continuous but not differentiable, and let \( S_2 \) be \( \{(p_1, \ldots, p_m) : \|\omega(p_1, \ldots, p_m)\| = \infty\} \). Then

(i) \( \omega(p_1, \ldots, p_m) \) is analytic on \( P \setminus (S_1 \cup S_2) \).

(ii) For \( s \in S_1 \), there are \( \epsilon, \delta (\epsilon < \delta) \), and \( t = (q_1, \ldots, q_m) \in P \setminus (S_1 \cup S_2) \) such that

\[
|s - t| < \delta, \ |\omega(s) - \omega(t)| < \epsilon.
\]

\[
I(t, \epsilon) = [q_1, q_1 + \epsilon] \times \cdots \times [q_m, q_m + \epsilon] \subset P \setminus (S_1 \cup S_2).
\]

Our basic tool is the following theorem.
Theorem 2.2 Let \( r \) be an even number greater than \( m \). Then \( \omega(p_1, \ldots, p_m) - E = 0 \) has solutions in \( P = [a_1, b_1] \times \cdots \times [a_m, b_m] \) if and only if

\[
\int_P \frac{dp_1 \cdots dp_m}{|\omega(p_1, \ldots, p_m) - E|^r} = \infty.
\]

Proof. Suppose that \( \omega(s) - E = 0 \) for \( s \in P \setminus (S_1 \cup S_2) \). Then we have

\[
\int_G \frac{dp_1 \cdots dp_m}{|\omega(p_1, \ldots, p_m) - E|^r} = \infty,
\]

where \( G \) is a rectangle satisfying \( s \in G \subset P \setminus (S_1 \cup S_2) \) [2].

Next, suppose that \( \omega(s) - E = 0 \) for \( s \in S_1 \). Take \( \epsilon \) and \( t = (q_1, \ldots, q_m) \in P \setminus (S_1 \cup S_2) \) satisfying (1) and (2). By the Taylor expansion of \( \omega(p_1, \ldots, p_m) - E \), we have

\[
\omega(p_1, \ldots, p_m) - E = \omega(q_1, \ldots, q_m) - E + \sum_{i=1}^{m} (p_i - q_i) f_i
\]

near \( t \), where \( f_1, \ldots, f_m \) are analytic functions. Hence

\[
\int_{I(t, \epsilon)} \frac{dp_1 \cdots dp_m}{|\omega(p_1, \ldots, p_m) - E|^r} > \int_{I(t, \epsilon)} \frac{dp_1 \cdots dp_m}{(\epsilon + \epsilon \sum_{i=1}^{m} |f_i|)^r} > \frac{1}{\epsilon^{r-m}(1+C)^r} \to \infty \quad \text{(as} \ \epsilon \to 0),
\]

where \( C \) is a constant satisfying \( C > \max_{x \in I(t, \epsilon)} \{\sum_{i=1}^{m} |f_i(x)|\} \).

Conversely, if \( \omega(p_1, \ldots, p_m) - E = 0 \) has no solution in \( P \), then we have

\[
\int_P \frac{dp_1 \cdots dp_m}{|\omega(p_1, \ldots, p_m) - E|^r} < \infty.
\]

By the Monte Carlo method, we can estimate

\[
F(P, E) = \int_P \frac{dp_1 \cdots dp_m}{|\omega(p_1, \ldots, p_m) - E|^r} \approx \frac{\prod_{i=1}^{m} (b_i - a_i)}{L} \sum_{j=1}^{L} \frac{1}{|\omega(s_j) - E|^r},
\]

where \( s_1, \ldots, s_L \) are points selected at random in \( P \). If \( F(P, E) \) is extremely large, then we conclude that \( \omega(p_1, \ldots, p_m) - E = 0 \) has solutions in \( P \).

3 Algorithm

The procedure to evaluate \( p_1, \ldots, p_m \) that minimize \( \omega(p_1, \ldots, p_m) \) is as follow:
Step 1: Divide the interval \([E', E''\) expected to contain the minimum of \(\omega(p_1, \ldots, p_m)\) into \(n\) equal subintervals \([E_0 (= E'), E_1, \ldots, [E_{n-1}, E_n (= E'')\)]\).

Step 2: Select the minimum of \(\{E_i : F(P, E_i) > D\}\). We denote by \(E_k\) the minimum. Here \(D\) is a large number, which is empirically given.

Step 3: Repeat Steps 1-2 for \([E_{k-1}, E_k\)].

Step 4: Repeat Steps 1-3 until the subintervals arrive at the prescribed precision. We denote by \(E\) the final value.

Step 5: Divide \([a_1, b_1\) into \(n\) equal subintervals \([a_{10} (= a_1, a_{11}], \ldots, [a_{1n-1}, a_{1n} (= b)]\).

Step 6: Estimate \(F(P, E)\) for each \(P_i = [a_{i1-1}, a_{i1}] \times [a_2, b_2] \times \cdots \times [a_m, b_m]\) and select \([a_{i1-1}, a_{i1}]\) that gives the maximum of \(\{F(P_i, E)\}\).

Step 7: Repeat Steps 5-6 for \([a_{1i-1}, a_{1i}]\).

Step 8: Repeat Steps 5-7 until the subintervals arrive at the prescribed precision. We denote by \([a_{1t-1}, a_{1t}]\) the final subinterval.

Step 9: Substitute \(q_1 = (a_{1t-1} + a_{1t})/2\) for \(p_1\) in \(\omega(p_1, \ldots, p_m)\).

Step 10: Set \(P = [a_2, b_2] \times \cdots \times [a_m, b_m]\) and

\[
F(P, E) = \int_P \frac{dp_2 \cdots dp_m}{|\omega(q_1, p_2, \ldots, p_m) - E|^r},
\]

where \(r\) is an even number greater than \(m - 1\).

Step 11: Repeat Steps 5-10 for \(p_2, \ldots, p_{m-1}\) and Steps 5-9 for \(p_m\).

References


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