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Stochastic Method for Calculating Wave Functions

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A relationship between the Boltzmann transport equation for a point in $3n$-dimensional configuration space executing random motion and the Schrödinger wave equation for n electrons is investigated. It is shown that wave functions and related quantities for the ground and excited states of atomic systems may be calculated with a stochastic computer program by incorporating the Pauli exclusion principle into the stochastic formalism. Stochastic calculations are presented for the ground state of hydrogen and for the ${}^1S$ and ${}^3S$ states of helium.

I. INTRODUCTION

INVESTIGATIONS of the relationships between the Schrödinger wave equation and the Boltzmann transport equation have led to numerous important results,[1–13] such as interpretations of the Schrödinger equation in terms of the Brownian motion of a diffusing particle, connections between quantum and classical statistical mechanics, and stochastic methods for calculating ground-state wave functions. It is the purpose of this paper to develop further these results by explicitly incorporating the Pauli exclusion principle into the stochastic formalism, and by calculating wave functions not only for the ground state of atoms but also for excited states. Let us start by considering the Boltzmann equation[14] for the random motion of a point in $3n$-dimensional configuration space:

$$\boldsymbol{\omega}\cdot \operatorname{grad} f(\mathbf{x},\boldsymbol{\omega})+[p_s(\mathbf{x})+p_a(\mathbf{x})]f(\mathbf{x},\boldsymbol{\omega}) = S(\mathbf{x},\boldsymbol{\omega})+\int d\boldsymbol{\omega}' f(\mathbf{x},\boldsymbol{\omega}')p(\boldsymbol{\omega}'\rightarrow\boldsymbol{\omega};\mathbf{x}), \quad (1)$$

where $f(\mathbf{x},\boldsymbol{\omega})d\boldsymbol{\omega}$ is the probability that a point in $3n$-dimensional configuration space is traveling within the differential solid angle $d\boldsymbol{\omega}$ around the direction $\boldsymbol{\omega}$ and crosses a unit area (normal to $\boldsymbol{\omega}$) at position $\mathbf{x}$ in unit time. Since the areas and solid angles are those of $3n$-dimensional configuration space, the angular flux $f(\mathbf{x},\boldsymbol{\omega})$ has the dimensions $l^{-3n+1}t^{-1}$. The probability per unit time of introducing a point at position $\mathbf{x}$ in the $3n$-dimensional volume element $d\mathbf{x}$ with a direction of motion within the $3n$-dimensional solid angle $d\boldsymbol{\omega}$ about $\boldsymbol{\omega}$ is denoted by the source term $S(\mathbf{x},\boldsymbol{\omega})d\mathbf{x}d\boldsymbol{\omega}$, and the corresponding probability per unit time of removing the point is given by the absorption term $p_a(\mathbf{x})f(\mathbf{x},\boldsymbol{\omega})d\mathbf{x}d\boldsymbol{\omega}$, where $p_a(\mathbf{x})$ is the probability per unit distance for absorption. Let $p_f(\mathbf{x})$ be the probability per unit distance that a randomly moving point in configuration space will fission, that is, produce another randomly moving point. For this case, the source term is proportional to the angular flux,

$$S(\mathbf{x},\boldsymbol{\omega})=p_f(\mathbf{x})f(\mathbf{x},\boldsymbol{\omega}), \quad (2)$$

and (1) becomes an eigenvalue problem. The fission and absorption probabilities may be combined to give a net generation term

$$p_g(\mathbf{x})=p_f(\mathbf{x})-p_a(\mathbf{x}). \quad (3)$$

Thus, when $p_g(\mathbf{x})$ is negative, (3) is the probability per unit distance that a point in configuration space will disappear, and when $p_g(\mathbf{x})$ is positive, (3) is the probability per unit distance that a new point will be generated.

The probability per unit distance that a point of configuration space traveling in the direction $\boldsymbol{\omega}$ at position $\mathbf{x}$ will have a scattering collision in which the final direction of motion is within $d\boldsymbol{\omega}'$ about $\boldsymbol{\omega}'$ is denoted by $p(\boldsymbol{\omega}\rightarrow\boldsymbol{\omega}';\mathbf{x})d\boldsymbol{\omega}'$. The probability per unit distance that a scattering collision will occur is obtained by integrating $p(\boldsymbol{\omega}\rightarrow\boldsymbol{\omega}';\mathbf{x})$ over all final directions:

$$p_s(\mathbf{x})=\int p(\boldsymbol{\omega}\rightarrow\boldsymbol{\omega}';\mathbf{x})d\boldsymbol{\omega}'. \quad (4)$$

It is convenient, although not essential, to assume that all final directions are equally probable. It is also frequently convenient to rewrite (1) in terms of the collision density

$$F(\mathbf{x},\boldsymbol{\omega})=p_s(\mathbf{x})f(\mathbf{x},\boldsymbol{\omega}), \quad (5)$$

where $F(\mathbf{x},\boldsymbol{\omega})d\mathbf{x}d\boldsymbol{\omega}$ is the probability per unit time that a collision will occur at $\mathbf{x}$, $\boldsymbol{\omega}$ within the configuration-space elements $d\mathbf{x}d\boldsymbol{\omega}$.

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If the probability of a scattering per unit distance traveled in configuration space is independent of the position of the moving point in configuration space, then $p_s = 1/\lambda_s$, where λ_s is the mean distance between scattering collisions. For the case of $\lambda_s \rightarrow 0$, we may expand $F(\mathbf{x}, \boldsymbol{\omega})$ in polynomials of the angular variable $\boldsymbol{\omega}$.[14] Neglecting terms of order λ_s^2 yields the diffusion equation of configuration space:

$$\lambda_s b \nabla^2 F(\mathbf{x}) + p_g(\mathbf{x}) F(\mathbf{x}) = 0, \tag{6}$$

where

$$F(\mathbf{x}) d\mathbf{x} = d\mathbf{x} \int F(\mathbf{x}, \boldsymbol{\omega}) d\boldsymbol{\omega} \tag{7}$$

is the probability per unit time that a collision will occur within the configuration-space volume element $d\mathbf{x}$ at $\mathbf{x}$, and where the value of the transport parameter b depends on the dimensionality of configuration space as well as on the functional form of $p(\boldsymbol{\omega} \rightarrow \boldsymbol{\omega}')$ and may be adjusted to correct for transport effects. For example, if configuration space is three-dimensional, if scattering is isotropic $(p(\boldsymbol{\omega} \rightarrow \boldsymbol{\omega}') = 1/4\pi)$, and if transport effects are negligible, then $b = \frac{1}{3}$.

The diffusion equation (6) of $3n$-dimensional configuration space

$$\sum_{i=1}^{3n} \frac{\partial^2 F(x_1, \cdots, x_{3n})}{\partial x_i^2} + \frac{p_s}{b} p_g(x_1, \cdots, x_{3n}) F(x_1, \cdots, x_{3n}) = 0 \tag{8}$$

has the same form as the Schrödinger equation in atomic units for a system of n identical particles in three-dimensional space,

$$\sum_{i=1}^{3n} \frac{\partial^2 \psi(x_1, \cdots, x_{3n})}{\partial x_i^2} + 2[E - V(x_1, \cdots, x_{3n})]\psi(x_1, \cdots, x_{3n}) = 0, \tag{9}$$

provided that

$$2[E - V(\mathbf{x})] = (p_s/b) p_g(\mathbf{x}), \tag{10}$$

and we draw a correspondence between the collision density $F(\mathbf{x})$ and the wave function $\psi(\mathbf{x})$.

II. PAULI EXCLUSION PRINCIPLE AND EXCITED STATES

In order that the spatial-spin wave function of a system of electrons represent a physical state, not only must its spatial part satisfy (9), but also it must conform to the Pauli exclusion principle, which states that it must be antisymmetrical when any pair of particles are interchanged. For a given spin state, this implies a symmetry condition for the spatial wave function $\psi(\mathbf{x})$. In the case of helium in the ^1S ground state, for example, the wave function $\psi(r_1, r_2, \theta)$, which depends on the radial distances of the two electrons from the origin and on the angle θ between them, is symmetrical,

$$\psi(r_1, r_2, \theta) = \psi(r_2, r_1, \theta), \tag{11}$$

whereas the wave function for the ^3S excited state is antisymmetrical,

$$\psi(r_1, r_2, \theta) = -\psi(r_2, r_1, \theta). \tag{12}$$

Although the collision density of a diffusing point in six-dimensional configuration space with $p_g(r_1, r_2, \theta)$ given by the potential energy function for the helium atom will satisfy (11), the antisymmetrical condition (12) presents a problem, especially since the collision density cannot be negative. This difficulty may be overcome and a solution satisfying (12) obtained by requiring the collision density to vanish at $r_1 = r_2$ and restricting attention to the region of configuration space where $r_2 > r_1$. Thus, the wave function for the ^3S state is given by

$$\psi(r_1, r_2, \theta) = F(r_1, r_2, \theta) \tag{13}$$

for $r_2 > r_1$, and by

$$\psi(r_1, r_2, \theta) = -F(r_2, r_1, \theta) \tag{14}$$

for $r_2 < r_1$. Therefore, by introducing an absorbing surface in configuration space, and restricting the motion of the diffusing point to one side of the surface, the Pauli principle can be satisfied.

III. DESCRIPTION OF THE COMPUTER PROGRAM

The algorithm programmed for the digital computer will now be described. A storage area S is reserved, with a capacity of 1000 $3n$-vectors, representing previously occupied points in configuration space. S is initialized with 500 random configuration points and N, an integer variable denoting the number of configuration points stored, is set initially at 500. Whenever a point is added to or taken from S, N is incremented or decremented by 1, so that N provides a running measure of the number of configuration points in S. As will be seen, a criticality parameter c is adjusted while the program runs in order to maintain N at an equilibrium value of about 500. The last point is never removed from S, and no more than 1000 points are stored in S.

Let $\mathbf{x}^t$ denote the configuration vector at the tth step with the origin corresponding to the nucleus, let x_1^t, x_2^t, and x_3^t denote the Cartesian coordinates of the first electron, etc. Given $\mathbf{x}^t$, the configuration point $\mathbf{x}^{t+1}$ is obtained by executing a random step in $3n$-space. This is achieved by setting

$$\mathbf{x}^{t+1} = \mathbf{x}^t + \boldsymbol{\xi}^t, \tag{15}$$

where $\boldsymbol{\xi}^t$ is a $3n$-vector whose components are independent random variables. In the program described, the components of $\boldsymbol{\xi}^t$ are uniformly distributed over the interval $[-2\lambda, 2\lambda]$, where λ is a fixed step-size parameter equal in this case to the average size of a step. Other distributions of $\boldsymbol{\xi}^t$ are possible, but this distribution was found adequate and is the simplest to program. A pseudorandom number generator is used to generate $\boldsymbol{\xi}^t$. Once $\mathbf{x}^{t+1}$ is determined, it is used to compile a histogram which will ultimately represent a stochastic approximation to the wave function.

The value of p_0, given by (10), at $\mathbf{x}^{t+1}$ now determines whether fission or absorption can take place. If $V(\mathbf{x}^{t+1})<E$, where E is the predetermined energy of the final solution, the point is in the fission region. Fission is taken to be binary, so that if fission occurs the point $\mathbf{x}^{t+1}$ is entered into the storage area and N is increased by 1. The ratio of the probability of generating a new point to the probability of scattering is given by $c[E-V(\mathbf{x})]$, where c is a criticality parameter whose determination is discussed below.

If $V(\mathbf{x}^{t+1})>E$, the point is in the absorption region. In this case, the ratio of the probability of absorption to that of scattering is given by $c[V(\mathbf{x})-E]$. If absorption takes place, the most recently added point is taken from S and a new random walk continues from that point. This point is deleted from S and N decreased by 1. If absorption does not occur the random walk continues from $\mathbf{x}^{t+1}$.

The value of c required to maintain equilibrium is initially unknown. A mechanism is incorporated into the program which decreases c if N increases and *vice versa.* Thus, if points begin to accumulate in the storage area, a decrease in c tends to decrease the rate of fission and hence stop the buildup of points. The following linear relation for varying c was used with the result that N stayed between 400 and 600 almost all the time:

$$c=c_0(2-N/500). \tag{16}$$

A value of c_0 which is only a rough estimate is used on the first run, and subsequently refined. It was found that the critical value of c was determined precisely enough after a few short runs of the same program so that a constant value of c could be used thereafter with no feedback mechanism at all.

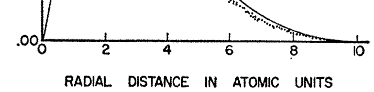

FIG. 1. Stochastic and exact collision density for the ground-state hydrogen atom. The stochastic results were obtained after 6 minutes execution time on the IBM 7094 and 4×10^5 collisions with $\lambda=\frac{1}{8}$.

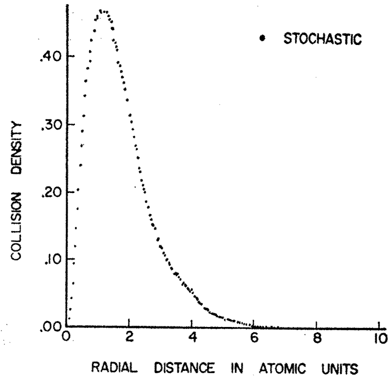

FIG. 2. Stochastic collision density for either electron of the ground-state helium atom. These results were obtained after 6 minutes execution time and 2×10^5 collisions with $\lambda=\frac{1}{8}$.

The algorithm described above is appropriate for the ground state of an n electron atom, without regard to the Pauli exclusion principle. In order to incorporate the exclusion principle in the case of the ^3S state of helium, the constraint $r_1<r_2$ is applied. This is done by comparing r_1 with r_2 at each newly generated point in configuration space. If $r_1>r_2$, the point is disregarded and the program continues as if an absorption had taken place.

IV. DISCUSSION OF RESULTS

Four separate cases were considered, each of increasing complexity. The simplest system treated was that of a single electron moving in a Coulombic field. Fig. 1 shows both the collision density $F(r)$ resulting from a six-minute stochastic program, and the exact distribution $\phi(r)=4\pi r^2\psi(r)=\frac{1}{2}r^2e^{-r}$. All stochastic results reported in this section were obtained from runs of approximately six minutes on the IBM 7094 digital computer. Here $F(r)dr$ is the probability that a collision will occur between the radial distances r and $r+dr$, and the wave function $\psi(r)$ is a solution of the Schrödinger equation of the ground-state hydrogen atom; the curves are normalized so that the area under each is unity. A comparison between the stochastic result $F(r)$ and the exact result $\phi(r)$ indicates satisfactory agreement. Deviations of $F(r)$ from $\phi(r)$ may be attributed to stochastic fluctuations, transient effects of the initial distribution of points in storage, and transport effects.

The ground state of the helium atom was considered next, and it was found that the repulsive interaction between the two electrons was easily incorporated into the stochastic program. Stochastic results for the collision density of either election are presented in Fig. 2. These calculations are consistent with other independent six minute runs of the same problem.

In order to check the validity of the procedure for incorporating the Pauli exclusion principle into the stochastic formalism, the ^3S state of helium was treated with no interaction between the electrons, and the

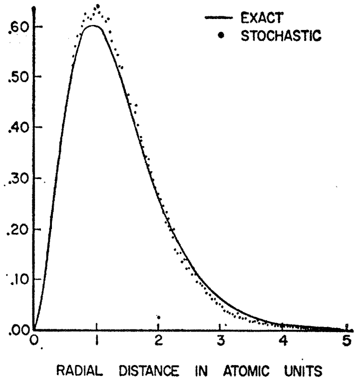

FIG. 3. Stochastic and exact collision density for the inner electron of the ^3S state of the helium atom without the repulsive Coulombic interaction between electrons. The stochastic results were obtained after 6 minutes execution time and 2×10^5 collisions with $\lambda=\frac{1}{8}$.

stochastic results compared with the exact results, which are known in this case:

$$\psi(r_1,r_2)=C[\psi_{1s}(r_1)\psi_{2s}(r_2)-\psi_{2s}(r_1)\psi_{1s}(r_2)], \qquad (17)$$

where $\psi_{1s}(r)$ and $\psi_{2s}(r)$ are the one-particle wave functions for the 1*s* and 2*s* states, respectively, and C is a constant of normalization. A convenient comparison between the exact and stochastic results may be made by integrating (17) over r_2 from $r_2=r_1$ to $r_2=\infty$:

$$\Phi(r_1)=4\pi r_1\int_{r_1}^{\infty}\psi(r_1,r_2)4\pi r_2 dr_2 \qquad (18)$$

$$=C[\phi_a(r_1)B(r_1)-\phi_b(r_1)A(r_1)], \qquad (19)$$

where

$$\phi_a(r)=4r^2e^{-2r}, \qquad (20)$$

$$\phi_b(r)=\tfrac{1}{4}(r^3-r^2)e^{-r}, \qquad (21)$$

$$A(r)=(2r^2+2r+1)e^{-2r}, \qquad (22)$$

$$B(r)=\tfrac{1}{4}(r^3+2r^2+4r+4)e^{-r}, \qquad (23)$$

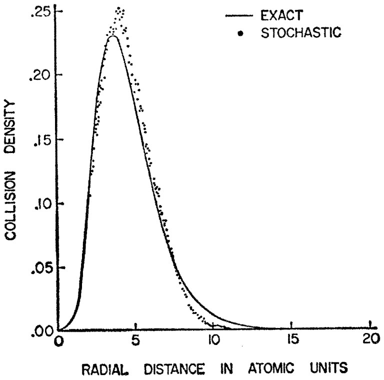

FIG. 4. Stochastic and exact collision density for the outer electron of the ^3S state of the helium atom without the repulsive Coulombic interaction between electrons. The stochastic results were obtained after 6 minutes execution time and 2×10^5 collisions with $\lambda=\frac{1}{8}$.

and where C is given by the normalization condition

$$\int_0^{\infty}\Phi(r_1)dr_1=1. \qquad (24)$$

In terms of the stochastic formalism, $\Phi(r_1)$ is the probability per unit radial distance that the inner particle will have a collision at r_1. Similarly, if we integrate (17) over r_1 from $r_1=0$ to $r_1=r_2$, we obtain

$$\Psi(r_2)=4\pi r_2\int_0^{r_2}\psi(r_1,r_2)4\pi r_1 dr_1 \qquad (25)$$

$$=\phi_b(r_2)[1-A(r_2)]-\phi_a(r_2)[1-B(r_2)], \qquad (26)$$

which is the probability per unit radial distance that the outer particle will have a collision at r_2. Results obtained from a six-minute computer run are given in Figs. 3 and 4, and a comparison with the exact results again indicates satisfactory agreement. Stochastic calculations for the ^3S state of helium were obtained by adding the repulsive Coulombic potential between the two electrons to the program; results from a six-minute computer run are given in Fig. 5.

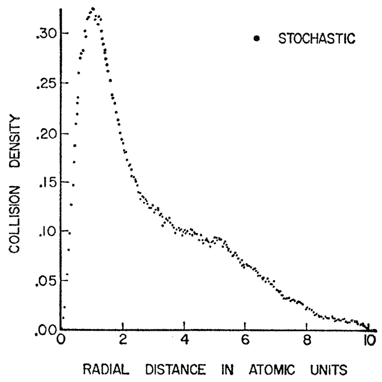

FIG. 5. Stochastic collision density for the ^3S state of helium. Shown is the sum of the collision densities of the inner and outer electrons. These results were obtained after 6 min execution time and 2×10^5 collisions with $\lambda=\frac{1}{8}$.

A more detailed analysis of stochastic, transient, and transport effects is under way. Future investigations will be concerned with the application of this method to more complex atoms, and to molecules.

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