PHYSICAL REVIEW A VOLUME 51, NUMBER 5 MAY 1995

Time-dependent unrestricted Hartree-Fock theory for the multiphoton ionization of atoms

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(Received 14 November 1994)

Time-dependent unrestricted Hartree-Fock (TDUHF) theory is formulated for the multiphoton ionization of a model atom. The single-particle states are nonorthogonal and the quantum variational principle requires additional normalization terms. For a model He atom, the three-dimensional (3D) electrostatic interaction is replaced by a 1D soft-core interaction that allows the construction of the two-electron atom in only two dimensions. The resulting 1D formulation of the TDUHF equations contains numerous exchange and overlap terms. The TDUHF multiphoton ionization rates are found to be in better agreement with the results of a direct solution of the time-dependent Schrödinger equation on a 2D lattice than the rates predicted by a 1D formulation of the standard TDHF equations.

PACS number(s): 32.80.Rm

I. INTRODUCTION

A good starting place for understanding correlation effects in atomic dynamics is the study of the multiphoton ionization of divalent atoms. The direct solution of the time-dependent Hartree-Fock (TDHF) equations, which has been used for many years to study heavy-ion collisions in nuclear physics [1–3], has been recently applied to calculate multiphoton ionization rates of the He atom [4,5]. The standard formulation of the full TDHF method, however, leads to unphysical and ambiguous ionization rates due to difficulties in describing the breakup of a two-electron ground state described by a single Slater determinant. In reality the standard TDHF method is a time-dependent restricted Hartree-Fock (TDRHF) theory, which has problems describing breakup reactions.

In this paper we formulate a time-dependent unrestricted Hartree-Fock (TDUHF) theory for the multiphoton ionization of atoms. Before embarking on a solution for the full 6D He atom, we first reduced the dimensionality of the problem from 6 to 2 by replacing the three-dimensional (3D) electrostatic interaction by a 1D soft-core interaction. This model two-electron system has been previously employed to study the multiphoton ionization of He [6], the multiphoton detachment of H^- [7,8], the autoionization of He* [9,10], and the multiphoton ionization of H_2 [11]. The dimensional reduction allows a relatively straightforward derivation of both the TDRHF and TDUHF equations for the multiphoton ionization of the He atom. At the same time the validity of the formulations may be checked against an "exact" time-dependent solution of the model on a 2D lattice. We find that the present formulation of the TDUHF method leads to a breakup of the ground state of He which is physically reasonable and in good agreement with the 2D lattice calculations. The various time-dependent theories are developed in Sec. II, numerical methods are outlined in Sec. III, multiphoton ionization results are presented in Sec. IV, and a summary is found in Sec. V.

II. THEORY

The Hamiltonian for the model He atom is given by

$$H_0 = -\frac{1}{2}\frac{d^2}{dx^2} - \frac{1}{2}\frac{d^2}{dy^2} - \frac{Z}{\sqrt{c+x^2}} - \frac{Z}{\sqrt{c+y^2}} + \frac{1}{\sqrt{c+(x-y)^2}} , \qquad (1)$$

where x and y are the coordinate positions of each electron, a nucleus of charge $Z = 2$ is located at $x = y = 0$, and c is an arbitrary constant used to soften the singularity of the potential. To study multiphoton absorption processes, we add the "length" gauge potential:

$$V = E(t)(x+y)\sin(\omega t) , \qquad (2)$$

where $E(t)$ is the amplitude and ω is the frequency of the electromagnetic field. The total Hamiltonian is $H = H_0 + V$.

For a total wave function constructed from orthogonal orbitals, the variational principle for the time-dependent Schrödinger equation is given by

$$i\left\langle \delta\psi \middle| \frac{\partial\psi}{\partial t} \right\rangle = \langle \delta\psi | H | \psi \rangle . \qquad (3)$$

To derive the time-dependent restricted Hartree-Fock equations for the ground state of the model He atom in an electromagnetic field, we start with the symmetrized product:

$$\psi(x,y,t) = u(x,t)u(y,t) . \qquad (4)$$

Total antisymmetrization of the wave function is obtained by multiplying the symmetric space function of Eq. (4) by an antisymmetric spin function. Upon substitution of Eq. (4) into Eq. (3), the variationally derived differential equation for the single-particle orbital, $u(x,t)$, is given by

$$i\frac{\partial u}{\partial t} = hu \ , \tag{5}$$

where

$$h = f + \langle u|g|u\rangle \ . \tag{6}$$

The one- and two-particle operators in Eq. (6) are given by

$$f = -\frac{1}{2}\frac{d^2}{dx^2} - \frac{Z}{\sqrt{c+x^2}} + E(t)x\sin(\omega t) \ , \tag{7}$$

and

$$g = \frac{1}{\sqrt{c+(x-y)^2}} \ . \tag{8}$$

The matrix element of the g operator in Eq. (6) is a direct potential term. The frozen-core TDRHF method replaces $\langle u|g|u\rangle$ in Eq. (6) by $\langle u_0|g|u_0\rangle$ involving the single-particle orbital $u(x,t=0)$.

For a total wave function constructed from nonorthogonal orbitals, the variational principle for the time-dependent Schrödinger equation is given by [12]

$$i\left\langle \delta\psi\middle|\frac{\partial\psi}{\partial t}\right\rangle = \langle\delta\psi|H|\psi\rangle + N\langle\delta\psi|\psi\rangle \ , \tag{9}$$

where

$$N = \frac{i\langle\psi|\frac{\partial\psi}{\partial t}\rangle - \langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \ . \tag{10}$$

To derive the time-dependent unrestricted Hartree-Fock equations for the ground state of the model He atom in an electromagnetic field, we start with the symmetrized product:

$$\psi(x,y,t) = \sqrt{\frac{1}{2}}(u(x,t)v(y,t) + v(x,t)u(y,t)) \ . \tag{11}$$

Total antisymmetrization of the wave function is again obtained by multiplying the symmetric space function of Eq. (11) by an antisymmetric spin function. Upon substitution of Eq. (11) into Eq. (9), the variationally derived differential equations for the nonorthogonal single-particle orbitals, $u(x,t)$ and $v(y,t)$, are given by

$$i\frac{\partial u}{\partial t} = h_{11}u + h_{12}v \ , \tag{12}$$

$$i\frac{\partial v}{\partial t} = h_{21}u + h_{22}v \ , \tag{13}$$

where

$$h_{11} = f + N + \frac{\langle v|f|v\rangle + \langle v|g|v\rangle - \lambda^*\langle u|f|v\rangle - \lambda^*\langle u|g|v\rangle + i\lambda^*\langle u|\frac{\partial v}{\partial t}\rangle}{1-\lambda^*\lambda} \ , \tag{14}$$

$$h_{12} = \frac{\langle v|f|u\rangle + \langle v|g|u\rangle - \lambda^*\langle u|f|u\rangle - \lambda^*\langle u|g|u\rangle - i\langle v|\frac{\partial u}{\partial t}\rangle}{1-\lambda^*\lambda} \ , \tag{15}$$

$$h_{21} = \frac{\langle u|f|v\rangle + \langle u|g|v\rangle - \lambda\langle v|f|v\rangle - \lambda\langle v|g|v\rangle - i\langle u|\frac{\partial v}{\partial t}\rangle}{1-\lambda^*\lambda} \ , \tag{16}$$

$$h_{22} = f + N + \frac{\langle u|f|u\rangle + \langle u|g|u\rangle - \lambda\langle v|f|u\rangle - \lambda\langle v|g|u\rangle + i\lambda\langle v|\frac{\partial u}{\partial t}\rangle}{1-\lambda^*\lambda} \ . \tag{17}$$

The matrix elements of the f operator are c numbers, while the matrix elements of the g operator are direct and exchange potential terms. The normalization term is given by

$$N = \frac{i\lambda\langle v|\frac{\partial u}{\partial t}\rangle + i\lambda^*\langle u|\frac{\partial v}{\partial t}\rangle}{1+\lambda^*\lambda} - E \ , \tag{18}$$

where the total energy is given by

$$E = \frac{\langle u|f|u\rangle + \langle v|f|v\rangle + \lambda^*\langle u|f|v\rangle + \lambda\langle v|f|u\rangle + \langle uv|g|uv\rangle + \langle uv|g|vu\rangle}{1+\lambda^*\lambda} \ . \tag{19}$$

In the derivation of the TDUHF equations we have assumed that $\langle u|u\rangle = \langle v|v\rangle = 1$ and that $\lambda = \langle u|v\rangle \neq 0$. Equations (12)–(17) may be used to construct a matrix equation for the time-dependent quantities $\langle v|\frac{\partial u}{\partial t}\rangle$ and $\langle u|\frac{\partial v}{\partial t}\rangle$. Solving that equation we find that

$$\left\langle v\middle|\frac{\partial u}{\partial t}\right\rangle = \frac{q_1}{2i} + \frac{(\lambda^*)^2 q_2}{2i} \ , \tag{20}$$

$$\left\langle u\middle|\frac{\partial v}{\partial t}\right\rangle = \frac{(\lambda)^2 q_1}{2i} + \frac{q_2}{2i} \ , \tag{21}$$

where

$$q_1 = \langle v|f|u\rangle - \lambda^* E + \frac{\lambda^*\langle v|f|v\rangle + \langle vv|g|vu\rangle - (\lambda^*)^2\langle u|f|v\rangle - \lambda^*\langle uv|g|vu\rangle}{1-\lambda^*\lambda} + \frac{\langle v|f|u\rangle + \langle vv|g|uv\rangle - \lambda^*\langle u|f|u\rangle - \lambda^*\langle uv|g|uv\rangle}{1-\lambda^*\lambda} \tag{22}$$

$$q_2 = \langle u|f|v\rangle - \lambda E + \frac{\lambda\langle u|f|v\rangle + \langle uu|g|uv\rangle - (\lambda)^2\langle v|f|u\rangle - \lambda\langle vu|g|uv\rangle}{1-\lambda^*\lambda} + \frac{\langle u|f|v\rangle + \langle uu|g|vu\rangle - \lambda\langle v|f|v\rangle - \lambda\langle uv|g|uv\rangle}{1-\lambda^*\lambda} \ . \tag{23}$$

Finally, the time-dependent Schrödinger equation:

$$i\frac{\partial\psi}{\partial t} = (H_0 + V)\psi \ , \tag{24}$$

may be solved directly for the time-dependent evolution of the ground state of the model He atom in an electromagnetic field.

III. NUMERICAL METHODS

The numerical solution of the TDRHF Eq. (5) and the TDUHF Eqs. (12) and (13) may be found by constructing a 1D mesh of equally spaced points (x_α). The one-particle operator is represented by

$$f u_\alpha = -\frac{1}{2}\left(\frac{u_{\alpha+1} + u_{\alpha-1} - 2u_\alpha}{(\Delta x)^2}\right) - \frac{Z u_\alpha}{\sqrt{c + x_\alpha^2}} + E(t) x_\alpha \sin(\omega t) u_\alpha \ , \tag{25}$$

where $\Delta x = x_\alpha - x_{\alpha-1}$. The two-particle potential terms are represented by

$$\langle v|g|v\rangle u_\alpha = \sum_\beta \frac{|v_\beta|^2 \Delta x \ u_\alpha}{\sqrt{c + (x_\alpha - x_\beta)^2}} \ , \tag{26}$$

while the c-number matrix elements are single or double trapezoidal rule integrations. The evolution of the 1D orbital in both real and imaginary time can be approximated either by the implicit expression

$$u_\alpha(t) = (L_x^+)^{-1} L_x^- u_\alpha(t_0) \ , \tag{27}$$

where

$$L^\pm{}_x = 1 \pm \frac{i\Delta t \ h}{2} \ , \tag{28}$$

or by the explicit expression

$$u_\alpha(t) = \exp(-i\Delta t \ h) u_\alpha(t_0) \ , \tag{29}$$

where $\Delta t = t - t_0$ is much less than ω^{-1}. A Taylor expansion of the exponential results in a series of matrix-vector multiplications. A matrix generalization of Eq. (29) is made for the coupled 1D orbitals found in the TDUHF method, while the implicit expression of Eq. (27) is used in the TDRHF method.

The numerical solution of the time-dependent Schrödinger equation [Eq. (24)] may be found by constructing a 2D lattice of equally spaced points (x_α, y_β). The atomic Hamiltonian operator is represented by

$$H_0\psi_{\alpha\beta} = -\frac{1}{2}\left(\frac{\psi_{\alpha+1,\beta} + \psi_{\alpha-1,\beta} - 2\psi_{\alpha\beta}}{(\Delta x)^2}\right) - \frac{1}{2}\left(\frac{\psi_{\alpha,\beta+1} + \psi_{\alpha,\beta-1} - 2\psi_{\alpha\beta}}{(\Delta y)^2}\right) - \frac{Z\psi_{\alpha\beta}}{\sqrt{c + x_\alpha^2}} - \frac{Z\psi_{\alpha\beta}}{\sqrt{c + y_\beta^2}} + \frac{\psi_{\alpha\beta}}{\sqrt{c + (x_\alpha - y_\beta)^2}} \ , \tag{30}$$

while the electromagnetic operator is represented by

$$V\psi_{\alpha\beta} = E(t)(x_\alpha + y_\beta)\sin(\omega t)\psi_{\alpha\beta} \ . \tag{31}$$

The evolution of the 2D wave function in both real and imaginary time is approximated by the implicit expression:

$$\psi_{\alpha\beta}(t) = (L_x^+)^{-1}(L_y^+)^{-1} L_y^- L_x^- \psi_{\alpha\beta}(t_0) \ . \tag{32}$$

A 2D generalization of the explicit expression found in Eq. (29) may also be used.

IV. MULTIPHOTON IONIZATION RESULTS

Ground state wave functions and energies for a model He atom are shown in Fig. 1. The contour plots of the probability density are centered at the $x = y = 0$

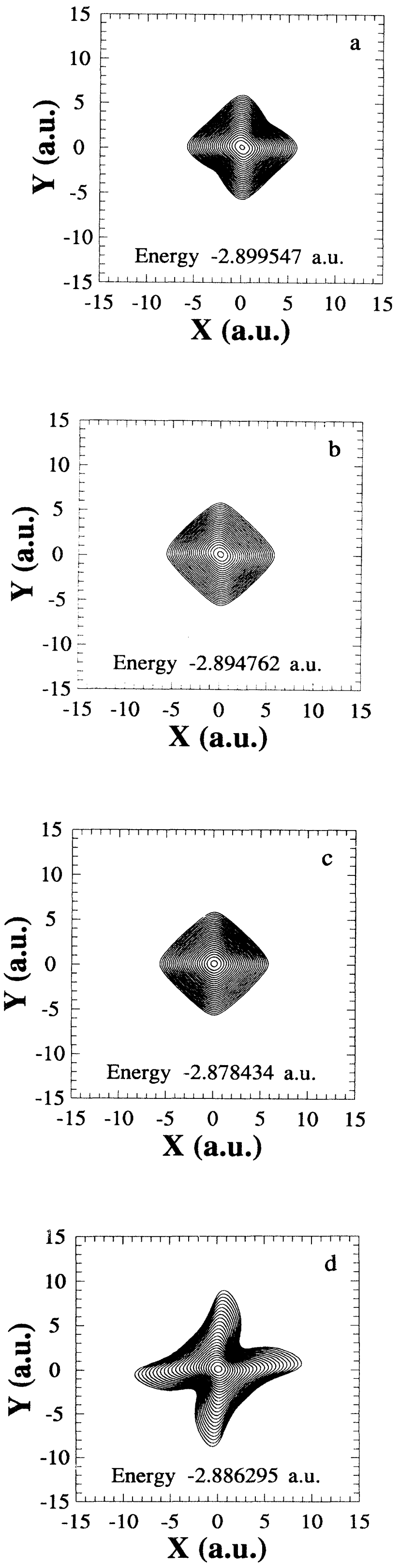

FIG. 1. Ground state wave functions for the model He atom. Contour maps of the probability density. The wave functions are from (a) 2D lattice solution, (b) UHF solution, (c) RHF solution, and (d) six-state CI solution.

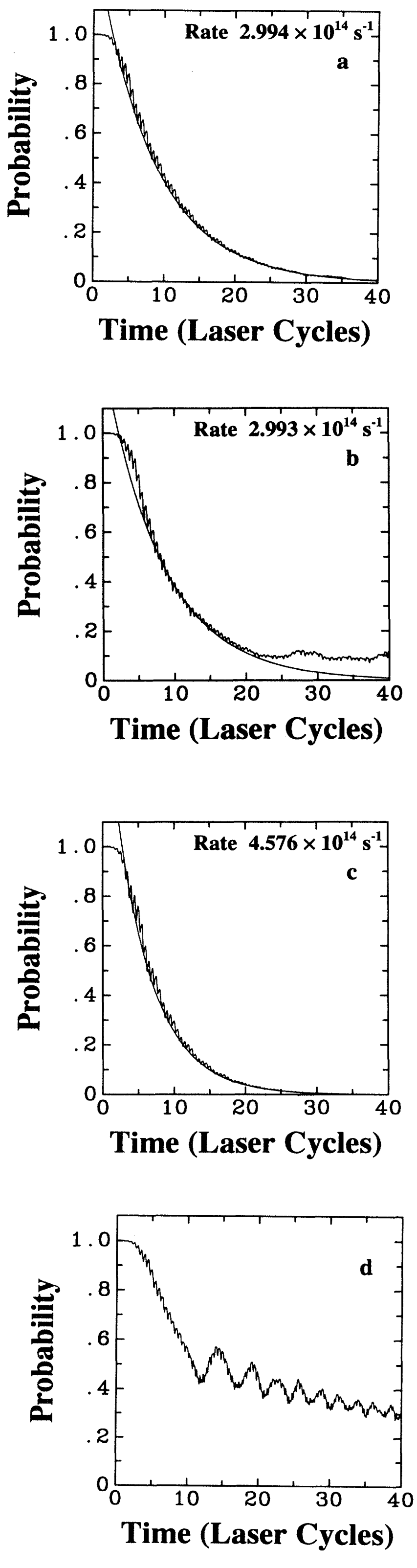

FIG. 2. Time evolution of the ground state probability for the three-photon (10.0 eV) ionization of the model He atom at an intensity of 1.0×10^{15} W/cm^2. The decay curves are for (a) 2D lattice solution, (b) TDUHF solution, (c) frozen-core TDRHF solution, and (d) full TDRHF solution.

minimum of the potential energy. The "exact" 2D lattice wave function is found by propagating an initial 2D Gaussian function in imaginary time using Eq. (32) with no electromagnetic field term. At each time step the total wave function is normalized to one. The UHF wave function is found by propagating an initial product wave function in imaginary time using a matrix generalization of Eq. (29) with no electromagnetic field terms. At each time step the individual orbitals u and v are normalized to one. Close to 1000 iterations are needed to fully converge the UHF ground state wave function. Along the way the UHF wave function seems to first converge to an excited state of the model He atom with the overlap $\langle u|v\rangle \sim 0$. At full convergence the overlap $\langle u|v\rangle = 0.84$ and the total energy is 0.13 eV above the 2D lattice results. These values compare well with a time-independent unrestricted Hartree-Fock calculation for the real He atom [13]. The RHF wave function is found by propagating an initial 1D Gaussian function in imaginary time using Eq. (27). At each time step the orbital is normalized to 1. The total RHF energy is found to be 0.57 eV above the 2D lattice results. A six-state configuration-interaction (CI) wave function is constructed by first obtaining the lowest energy eigenfunctions of the Hamiltonian:

$$h_0 = -\frac{1}{2}\frac{d^2}{dx^2} - \frac{Z}{\sqrt{c+x^2}} , \tag{33}$$

on a 1D grid of equally spaced points. The bound eigenfunctions are designated by ns. Even parity symmetric product states are then formed and a small basis set diagonalization is made to find the ground state of the model He atom. The six-state CI wave function shown in Fig. 1 is a linear combination of the $1s^2, 2s^2, 3s^2, 4s^2, 1s3s, 2s4s$ product states. Although the total CI energy is only 0.36 eV above the 2D lattice results, the wave function is not very good at large distances from the nucleus.

The electron-electron repulsion term of Eq. (1) is largest along a line in the xy plane at which $x = y$, and smallest along a line at which $x = -y$. The contour plots of the probability density for the 2D lattice wave function, as found in Fig. 1(a), mirror this feature of the potential. The contour lines are elliptical in shape with their major axis oriented along the line of smallest electron-electron repulsion. The contour plots of the probability density for the UHF wave function, as found in Fig. 1(b), are also elliptically shaped. The contours for the RHF wave function in Fig. 1(c), however, are circular, as befitting a strict central field calculation.

Once ground state wave functions for the model He atom are obtained, the various time-dependent equations may be propagated forward in real time with an electromagnetic field potential turned on using a linear ramp for the amplitude $E(t)$. The time evolution of the ground state probabilities are shown in Fig. 2 for an intensity of 1.0×10^{15} W/cm^2 and a photon energy of 10.0 eV, corresponding to three photon ionization of the atom. Least square fits to the decay curves yield the rate of depletion of the ground state, which in our case is equivalent to the multiphoton ionization rate of the atom. For cases in which the ground state is tuned to near resonance with an excited bound state, this equivalence is not true. There is very good agreement between the 2D lattice and TDUHF ionization rates. In both, the curve fitting begins at the end of the linear ramp at 5 laser cycles, while the fit for the TDUHF decay curve ends at 20 laser cycles. Beyond 20 laser cycles the TDUHF decay curve becomes sensitive to reflections from the grid boundary. The frozen-core TDRHF ionization rate is almost a factor of 2 larger than the 2D lattice results, while a meaningful ionization rate cannot be extracted from the full TDRHF decay curve. Three-photon ionization rates as a function of intensity for the model He atom are shown in Fig. 3. For a range of intensities the ionization rates for the 2D lattice and TDUHF methods are found to be in very good agreement, while the frozen-core TDRHF rates are always substantially larger. At smaller intensities than those shown in Fig. 3, numerical instabilities in the TDUHF method make an extraction of an ionization rate less reliable. The 2D lattice and frozen-core TDRHF methods, however, are still stable and provide a three-photon ionization rate which scales with the I^3 dependence predicted by perturbation theory.

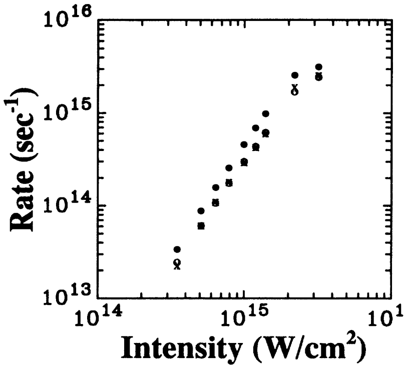

FIG. 3. Three-photon (10.0 eV) ionization rates for the model He atom. Open circles, 2D lattice solution, crosses, TDUHF solution, and solid circles, frozen-core TDRHF solution.

V. SUMMARY

Multiphoton ionization rates for a model He atom have been calculated using several computational methods. A direct solution of the time-dependent Schrödinger equation on a lattice should, in principle, be the most accurate method. A standard time-dependent Hartree-Fock method has difficulties in describing the breakup of a two-electron ground state when restricted to one orbital. The orbital tracking the photoionized electron is the same one that is used to calculate the screening potential. The outgoing electron thus sees a steadily increasing effective nuclear charge. The TDRHF difficulty may be partly mitigated by freezing the potential so that the outgoing electron sees a constant effective nuclear charge. Another approach is to formulate a time-dependent unrestricted Hartree-Fock method that describes the breakup of a two-electron ground state using two active orbitals. The photoionized electron is described by one orbital, while the second orbital is free to describe an electron which lingers about to screen the nuclear charge in a proper manner. The second electron may later also ionize leading to sequential double ionization, or in rare cases both electrons may ionize simultaneously. A furthur study of simultaneous double ionization would probe the true essence of the two-electron correlation problem. A drawback to the TDUHF method is the increased complexity of the time-dependent coupled equations for the two orbitals; exchange terms, normalization terms, and overlap factors must all be taken into account. Our calculations for the multiphoton ionization of a model He atom have shown that the agreement between the "exact" 2D lattice method and the TDUHF method is very good for total rates. In the future we plan to furthur investigate the strengths and weaknesses of the TDUHF method when applied to more detailed ionization dynamics and to develop a time-dependent multiconfiguration Hartree-Fock method which may prove numerically more stable. The ultimate goal is the consideration of real (full dimensional) divalent atoms and the development of a general TDHF method which would compete favorably with a direct solution of the time-dependent Schrödinger equation.

ACKNOWLEDGMENTS

We would like to thank Dr. Donald C. Griffin of Rollins College and Dr. Francis Robicheaux of Auburn University for many useful discussions. This work was supported in part by the National Science Foundation under Grant No. PHY-9122199 with Auburn University. Computational work was carried out at the National Energy Research Supercomputer Center in Livermore, California and the Alabama Supercomputer Center in Huntsville, Alabama.

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