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Solutions to the time-dependent three-dimensional Schrödinger equation: Atoms in intense electric fields

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We develop a technique for solving the time-dependent three-dimensional Schrödinger equation by expanding in terms of a set of Volkov functions and converting to a system of first-order temporal equations. Solutions are obtained through standard multivalue propagation schemes. We apply the method to several cases including the interaction of an intense, oscillating electric field with a model three-dimensional atomic system, observing the above-threshold ionization structure.

The advent of the new high-intensity lasers has focused considerable theoretical attention on the interactions of intense electromagnetic (EM) fields with atoms.[1] When the electric field is much weaker than the atomic binding, the usual time-dependent (TD) perturbation expansion in terms of the stationary states of the atomic Hamiltonian appears adequate. On the other hand, for extremely intense fields, a more natural expansion basis becomes the Volkov states with the atomic potential serving as a perturbation. In the intermediate regime corresponding to the intensity range of many current lasers, the two components are comparable in strength, and we must treat the EM and atomic fields on equal footing. In this case, we are usually forced to solve the full TD Schrödinger equa- For one spatial dimension (1D), we encounter a particularly rich collection of methods, ranging from TD finite-difference[2,3] and finite-element[4] approaches to Floquet methods,[5] to Fourier-transform techniques,[6] to integral equations formulations[7] (a more complete listing appears elsewhere[2]). However, full temporal treatments of three-dimensional (3D) systems are much rarer and have basically been confined to finite-difference (FD) prescriptions[8] and Floquet analysis,[9,10] both of which bring powerful computational tools to bear on this difficult problem. In searching for other possible entries into this realm, we have explored a promising candidate in which we convert to a set of first-order temporal equations by expanding the wave function in 3D Volkov states. The method represents an extension of an earlier procedure[11] and has some similarities with the 1D approach of Dorr and Shakeshaft.[12] The basic electric field interaction is removed by the analytical basis leaving the atomic potential to provide the dominant coupling. Expansions in terms of Volkov states[13] have formed the basis of numerous other approaches, most notably the so-called Keldysh-Faisal-Reiss formulations (KFR).[14] While the various renditions of the KFR formulations can be iterated to an exact solution of the TD Schrödinger equation, the form usually employed involves various approximations and represents but a single iteration.[14(b)] Our particular approach corresponds to a fully converged iterative solution in the Volkov basis and is comparable to the 3D Floquet and FD results. For the multiphoton ionization of atoms, the Volkov expansion has possible advantages. As time passes, the distribution in momentum space concentrates around a few well-defined peaks, the usual signatures of "above-threshold ionization (ATI)." Therefore, we can selectively tighten the mesh about these isolated areas. On the other hand, in configuration space, we must enlarge the area spanned by the basis in order to follow the ever spreading wave packet. Like its 1D counterpart,[11] our approach is quite flexible and can handle general temporal and spatial dependencies of the field, being ideal for investigating various pulse shapes and other fugacious effects. Another advantage rests with the simplicity of the propagation algorithm. Since we need only advance first-order temporal equations, our highest-order processes are matrix-vector multiplications, which are particularly well suited to vector computers and the new multiprocessors. While the method is very general, we choose to illustrate its mechanics on a standard model[8,9] of atom intense-field interactions.

We begin by following the commonly trod path of converting second-order differential equations, depending on spatial and time coordinates $(\mathbf{r},t)$, into a coupled, first-order temporal set. We seek a solution to a 3D Schrödinger equation that represents the motion of an electron in an atomic potential V_a subject to a TD interaction V_E:

$$[-\tfrac{1}{2}\nabla^2+V_a(\mathbf{r})+V_E(\mathbf{r},t)]\psi(\mathbf{r}|t)=iD_t\psi(\mathbf{r}|t)\,, \quad (1)$$

where $D_t\equiv\partial/\partial t$ and ∇^2 is the usual Laplacian. In the dipole approximation for an oscillating electric field, the interaction term V_E has the form

$$V_E(\mathbf{r}|t)=\mathbf{E}(\mathbf{r}|t)\cdot\mathbf{r}\,, \quad (2)$$

with the electric field described by $\mathbf{E}(\mathbf{r}|t)=\mathbf{E}_0(t)f(\mathbf{r}|t)$ such that $\mathbf{E}_0(t)\equiv E_0\cos(\omega t)\hat{\mathbf{e}}$. We let E_0,ω, and T represent the maximum field strength, the frequency, and the period $(2\pi/\omega)$ of the oscillating electric field, respectively, $f(\mathbf{r}|t)$ determine the spatial and temporal behavior of this field, and $\hat{\mathbf{e}}$ represent the unit vector in the field direction. Since this particular model has become a cynosure for studying an atom in an intense laser field,[8,9,14] we feel justified in its use to demonstrate our approach.

We now expand the total system wave function in a basis $\{\phi_{\mathbf{k}}(\mathbf{r}|t)\}$ of a complete set of states as

$$\psi(\mathbf{r}|t)=\int a(\mathbf{k}|t)\phi_{\mathbf{k}}(\mathbf{r}|t)d\mathbf{k}\,. \quad (3)$$

The square modulus $|a(\mathbf{k}|t)|^2$ of an expansion coefficient gives the probability of finding the system in state $\mathbf{k}$ at time t. We select the basis to satisfy the following equation:

$$[-\tfrac{1}{2}\nabla^2+V_1(\mathbf{r}|t)-iD_t]\phi_{\mathbf{k}}(\mathbf{r}|t)=0. \quad (4)$$

These solutions form a complete set of basis states with the usual orthonormality property that $\langle\mathbf{k}'|\mathbf{k}\rangle=\delta(\mathbf{k}'-\mathbf{k})$ and are labeled by a "momentum" vector $\mathbf{k}$. We select the potential to remove as much of the dominant interaction as possible but to remain elementary enough to yield analytical or simple numerical solutions.

We derive an expression for the expansion coefficients by (i) substituting Eq. (3) into (1), (ii) multiplying through by $\phi_{\mathbf{k}'}(\mathbf{r}|t)^*$, (iii) integrating over the spatial coordinates $d\mathbf{r}$, and (iv) employing the orthonormality properties of the basis. The results of these manipulations yield

$$D_t a(\mathbf{k}'|t)=\int M(\mathbf{k}',\mathbf{k}|t)a(\mathbf{k}|t)d\mathbf{k}, \quad (5)$$

where

$$M(\mathbf{k}',\mathbf{k}|t)\equiv -i\int \phi_{\mathbf{k}'}(\mathbf{r}|t)^*[V_a(\mathbf{r})+\Delta V(\mathbf{r}|t)] \times\phi_{\mathbf{k}}(\mathbf{r}|t)d\mathbf{r}, \quad (6)$$

where $\Delta V=(V_E-V_1)$. Therefore, by determining the temporal evolution of the coefficients from Eq. (5), we can construct the solution at any time from Eq. (3).

For the intense field case, we choose the basis by setting V_1 to $\mathbf{E}_0(t)\cdot\mathbf{r}$. The solutions to Eq. (4) are the familiar Volkov states, $\phi_{\mathbf{k}}^v(\mathbf{r}|t)$, and have a precise analytical expression.[13] The coupling term now becomes the atomic potential and the difference between $\mathbf{E}_0$ and the actual form of the electric field $[\Delta V=(f-1)\mathbf{E}_0\cdot\mathbf{r}]$. For the case in which the field is uniform in space and purely oscillatory in time ($f=1$), the difference term vanishes, and the atomic potential alone provides the coupling. A similar condition arises for a spatially uniform field that can be considered constant over a prescribed time step. Since we can approximate any general temporal function by a series of such time steps, we can accurately represent realistic pulses by this simpler form of Eq. (6). We choose to operate in cylindrical coordinates $[\mathbf{r}=(z,\rho,\varphi)]$ since for the choice of the field polarization in the direction of the quantization axis $\hat{\mathbf{z}}$, the interaction term assumes a particularly simple form, namely $E_0\cos(\omega t)z$. In this case, the Volkov states become

$$\phi_{\mathbf{k}}^v(\mathbf{r}|t)\equiv\phi_{\kappa qm}(z\rho\varphi|t)=\chi_\kappa(z,t)\chi_{qm}(\rho,t)\chi_m(\varphi), \quad (7)$$

where $\chi_\kappa(z,t)$ is the 1D Volkov solution,[2] $\chi_{qm}(\rho,t)$ is proportional to the bessel function $J_m(q\rho)\exp(-iq^2t/2)$, and $\chi_m(\varphi)$ has the usual form $\exp(im\varphi)$. The states are labeled by three momentum components $\mathbf{k}=(\kappa,q,m)$, two continuous and one discrete, according to their associated spatial cylindrical coordinates. The total system wave function is then given in terms of this basis by Eq. (3) with expansion coefficients $a_{\kappa qm}(t)$. Since χ_κ has a precise 1D analogue, we gain valuable insight into the 3D case by investigating models with but one spatial dimension, especially in matters of mesh size, basis, and phenomenology.

In order to solve Eq. (5), we approximate the integrals by discrete quadratures and evaluate the coefficients at these prescribed points, thus converting to a set of matrix equations. Using n_κ quadrature points for the κ dimension and n_q in q, we obtain the following system of equations, whose solutions are the expansion coefficients:

$$D_t\underline{a}(t)=\underline{M}(t)\underline{a}(t). \quad (8)$$

The matrix $\underline{M}$ is of order $N_t=n_\kappa n_q n_m$, where n_m is the number of m values, with elements given by Eq. (6). The interaction term is V_a, the atomic potential, and the basis consists of the Volkov states [Eq. (7)]. The vector $\underline{a}$ is of length N_t with components $a_{\kappa qm}$. For the case of a spherically symmetric potential, these equations become block diagonal in the quantum number m. Therefore, for a given value of m, we need only solve a two-dimensional problem in momentum space ($N_t=n_\kappa n_q$). In practice, we usually propagate $b_{\mathbf{k}}(t)=a_{\mathbf{k}}(t)g(t)$, where the function $g(t)$ removes much of the oscillatory part. For this case, the off-diagonal coupling matrix elements become time independent and therefore need be calculated only once. We have made several basic simplifications to the general method: (i) the electric field is along the atomic quantization axis; (ii) the atomic potential is spherically symmetric; (iii) the spatial dependence of $f(\mathbf{r},t)$ is uniform; and (iv) the dipole approximation is invoked. We emphasize that these conditions can all be relaxed and in no way circumscribe the general procedure, although possibly leading to greater computational time.

We are now left with a coupled system of first-order temporal equations [Eq. (8)]. Since we are primarily interested in photoionization, we start the solution in a prescribed bound state of the atomic system, $\phi_a(\mathbf{r}|t_0)$, at time $t=t_0$. From this initial condition, we determine the starting values of the expansion coefficients $a_{\mathbf{k}}(t_0)$ by inverting Eq. (3). Once the initial values are known, we can use standard first-order propagation schemes to evolve the coefficients in time. We have tested a number of techniques including the Adams-Bashford,[15] the Bulirsch-Stoer,[15] the Gear,[16] and the second-order difference.[17] All perform effectively and efficiently with the Gear employed as a standard since stiff equations are sometimes encountered. The spatial integrals in the matrix elements are constructed by Simpson's rule and when appropriate by a judicious application of the Filon technique. The momentum meshes are selected as Gauss-Legendre quadratures and usually require between 20 and 50 points in each dimension. Therefore, we typically propagate first-order temporal equations of the order of 2000 for 10–20 cycles of the electric field. Such solutions generally require from 3 to 10 min of central processing unit time on a Cray-XMP computer, depending on the level of accuracy sought.

In order to illustrate this approach, we consider the ionization from an atomic potential of the form

$$V_a(\mathbf{r})=V_0\exp(-\lambda r)/r,$$

the standard Yukawa expression. The strength of the exponential coefficient only increases the effort in evaluating the spatial integrals in Eq. (6) but does not change the

basic form of the coupled temporal equations, which lie at the heart of this approach. Therefore, we can examine the most general features of the method by considering this special case. We also tune λ such that the potential supports but one bound state with symmetry $m=0$. This constraint is in no way severe, and to demonstrate this point, we have performed calculations on potentials with a variety of bound states. We select $\lambda=0.397$ and $V_0=1$ to yield a single bound s state at an energy $\varepsilon=-0.200$ hartrees. Therefore, the solution at $t=0$ begins in this bound state, $\phi_b(\mathbf{r})$. For this case, the ionization probability $P_i(t)$ is given by the simple expression: $1-|\langle\phi_b|\psi\rangle|^2$. The ionization probability per unit time then has the form $W_i(t)\equiv P_i(t)/t$. We select the κ and q meshes so as to place a preponderance of points in the vicinity of the suspected positions of the ATI peaks. Neglecting the shift in the bound state, we expect the peaks to emerge at energies E_n, given by $n\omega-\varepsilon-E_j$, where the final term is the famous jitter energy $[(E_0/2\omega)^2]$. In order to test the procedure, we performed a series of calculations for a weak field ($E_0=0.007$ a.u.) for single-photon ionization ($\omega>0.200$) and compared with perturbation theory. We found that $W_i(t)$ became a constant after about five cycles of the field and was in excellent agreement with the perturbation results. For example, at $t=10T$ we have from the 2D calculations for $\omega=0.21$, 0.25, and 0.30 that $W_i=2.8\times10^{-4}$, 5.5×10^{-4}, and 4.0×10^{-4}, respectively, while perturbation theory yields 2.7×10^{-4}, 5.9×10^{-4}, and 4.1×10^{-4}, respectively. These results were obtained with about 30 points in the q mesh and 50 in the κ. In many ways, the weak-field calculations are a particularly stringent test of this method. Since the expansion basis is selected to remove the electric field component, leaving the atomic potential to exert the principal coupling, the best regime for this method occurs when the oscillating electric field is comparable to, or stronger than, its atomic counterpart. In the weak-field limit, just the opposite extreme is reached with the atomic interaction playing the dominant role. Therefore, we are quite encouraged by the close agreement obtained in the field-perturbation limit.

We now present results in which the field becomes significantly larger.[18] We first investigate the case for $\omega=0.25$ ($T=25.1$ a.u. $=0.6$ fs), and $E_0=0.075$ a.u. (2.0×10^{14} W/cm^2). By five cycles of the field ($t=5T$), the system has almost completely ionized ($P_i>0.90$). At this stage, the packet has effectively cleared the range of the atomic potential. Since the atomic potential provides the only coupling in this case, the expansion coefficients with respect to the Volkov states no longer change—the system remains in a fixed distribution of the basis. In fact for this case, we can easily demonstrate that at a time that is a multiple of the field period ($t=nT$), the probability of finding the system in a particular Volkov state is the same as that to find it in a free-particle state ($E_0=V_a=0$). Therefore, the square modulus of the expansion coefficients at nT gives us important information on the energy distribution of the ionized electron. In Fig. 1, we plot the probability of finding the system in a given momentum state, $|a(t)|^2$, as a function of (κ,q) at ten periods into the ionization process. We note a particularly strong concentration of probability in two annuli approximately centered at $K\approx0.2$ and 0.7, where $K^2\equiv\kappa^2+q^2$. In order to make this identification more explicit, we perform a polar projection (K,θ) of the probability onto associated Legendre polynomials $P_{lm}(\theta)$ with $\tan\theta\equiv\kappa/q$. In Fig. 2, we display $P_K(t)$, which is $P_{Kl}(t)\equiv|a_{Kl0}(t)|^2$, summed over all l, at $t=10T$ as a function of K. Not surprisingly, we observe an ATI peak at $K\approx0.18$ whose character is principally $p(l=1)$ in nature, conforming to the dipole selection rule for single-photon absorptions. The slight additional lowering of the peak position (0.18 compared to 0.23) is usually ascribed to the ac Stark shift involving the bound level. We also observe a second ATI peak at $K\approx0.72$, which also has both s and d character. As we increase the electric field further, we observe that the ATI peaks shift to lower energies, and the first peak eventually disappears, qualitatively resembling the 1D findings.[2,3]

In summary, we have developed a general procedure for

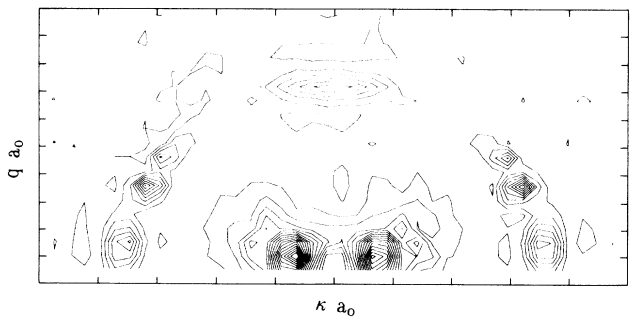

FIG. 1. Probability density $|a_{\kappa q}(t)|^2$ at $t=10T$ as a function of the two momenta κ and q for the Yukawa potential with $E_0=0.075$ a.u. and $\omega=0.25$. The κ axis extends from -0.8 to 0.8 in units of 0.2, while the q axis ranges from 0.0 to 0.8 in units of 0.1.

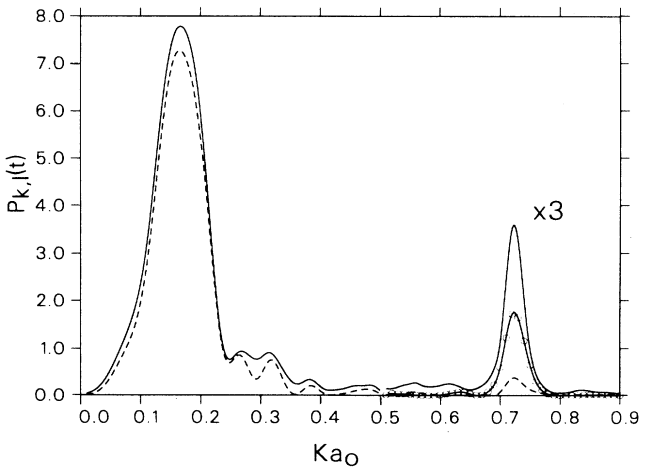

FIG. 2. Polar projection $P_{K,l}(t)$ of the density in Fig. 1 for $l=1$ (dashed line), $l=2$ (line with circles), and the sum over all l values (solid line) as a function of K. Second ATI peak has been enhanced by a factor of 3 in order to better display the components.

solving the three-dimensional, time-dependent Schrödinger equation by expanding the total system wave function in a basis designed to account for the dominant component of the interaction. We have applied the technique to an atom in an intense laser field and determined basic ionization properties as well as the ATI structure.

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[18]We have $n_q = 34$, distributed over (10,10,7,7) points in four regions: (0.0,0.5,1.0,3.0,7.0) and $n_x = 48$ with (5,8,8,6,8,8) points in seven regions: $(-5.0, -1.0, -0.5, -0.25, 0.25, 0.5, 1.0, 5.0)$. For the second-order difference, a typical time step is 0.0125 au, which can be larger for the Gear.