A systematic technique for conservatively discretizing the time dependent Schrödinger equation on an arbitrary structured grid is given. Spatial differencing is carried out by finite volumes, and temporal differencing is carried out semi-implicitly. It is shown that the resulting algorithm conserves probability to within a round-off error regardless of the grid geometry. The algorithm is efficient for both serial and parallel computation. The conservative nature of the algorithm, and its phase accuracy, are demonstrated for a bound state, and for a free state in an electromagnetic field. The ionization rate for a hydrogen atom in a strong electromagnetic field is computed, and compared with the rate from tunneling theory. The regime of validity of tunneling theory is clarified.

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or parabolic coordinates, in any number of dimensions up to three. Furthermore, the code can be said to support any coordinate system in the sense that introducing new coordinates is just a matter of modifying certain input parameters pertaining to the grid.

2. Spatial discretization by finite volumes

In order to difference the TDSE using finite volumes, all spatial derivatives need to be gathered into a total divergence. In the Coulomb gauge, the TDSE can be put in the form

$$\partial_t \psi + \nabla \cdot \mathbf{f} = i\mathcal{A} \psi$$

(2)

where

$$\mathbf{f} = \left( \mathbf{A} - \frac{i}{2} \nabla \right) \psi$$

(3)

and

$$\mathcal{A} = \Phi - \frac{A^2}{2}$$

(4)

Here, \(\psi\) is the wavefunction, \(\mathbf{A}\) is the vector potential, \(\Phi\) is the scalar potential, and atomic units (a.u.) are used throughout. The finite volume method consists of integrating Eq. (2) over the volume of a cell, and using the divergence theorem to calculate the time rate of change of \(\psi\) in terms of the flux through the cell walls. If \(\mathcal{A}\) were to vanish, this scheme would obviously conserve amplitude, since the flux through any cell wall would take from one cell exactly what it put in another. What is less obvious is that this scheme conserves probability when combined with the Cayley form of the time translation operator.

Let the numerical grid be defined as the union of a set of cells \(\Omega_{ijk}\), where \(i, j,\) and \(k\) index discrete values of the coordinates \(\xi(x, y, z), \eta(x, y, z),\) and \(\zeta(x, y, z),\) respectively. In particular, each cell corresponds to a region in parameter space defined by

$$\Omega_{ijk} = \left\{ \xi = \xi_{i-\frac{1}{2}}, \eta = \eta_{j-\frac{1}{2}}, \zeta = \zeta_{k-\frac{1}{2}} \right\}$$

(5)

where half-indexed quantities correspond to the average of the nearest integer indexed quantities. The only restriction on the coordinate system is that the basis vectors be everywhere orthogonal. Then the metric tensor is fully characterized by the three scale factors \(h_i, h_j,\) and \(h_k\). The volume of a cell is

$$V_{ijk} = \int_{\Omega_{ijk}} d\xi d\eta d\zeta h_i h_j h_k$$

(6)

The area of a cell wall is most easily expressed after choosing a particular plane. For example, let \(S^i_{-\frac{1}{2}jk}\) be the area of the cell wall defined by \( \left\{ \xi = \xi_{i-\frac{1}{2}} \right\} \cap \Omega_{ijk} \). Then

$$S^i_{-\frac{1}{2}jk} = \int_{\eta_{j-\frac{1}{2}}}^{\eta_{j+\frac{1}{2}}} \int_{\zeta_{k-\frac{1}{2}}}^{\zeta_{k+\frac{1}{2}}} d\eta d\zeta h_i h_j h_k$$

(7)

The other two cases, \(S^j_{-\frac{1}{2}ik}\) and \(S^k_{-\frac{1}{2}ij}\), are similar.

Suppose that what is known at the beginning of each time step is the amplitude averaged over each cell volume:

$$\psi_{ijk} = \frac{1}{V_{ijk}} \int_{\Omega_{ijk}} d\xi d\eta d\zeta h_i h_j h_k \psi$$

(8)

Then, integrating Eq. (2) over the cell volume gives

$$V_{ijk} \left( \partial_t - i\mathcal{A}_{ijk} \right) \psi_{ijk} = -\int_{\partial\Omega_{ijk}} d\mathbf{S} \cdot \mathbf{f}$$

(9)

where \(\partial\Omega\) is the cell boundary, and \(d\mathbf{S}\) is the element of surface area. In order to discretize the surface integral, an estimate for the flux density \(\mathbf{f}\) integrated over a cell wall is needed. Due to the use of an orthogonal basis, only one component is needed per cell wall. If the wall averages are formed by averaging over adjacent cells, the wall fluxes are

$$F^i_{-\frac{1}{2}jk} = -\frac{i}{2} \frac{\psi_{ijk} - \psi_{i-1jk}}{h_i (\xi_i - \xi_{i-1})} + \frac{A^2}{2} (\psi_{i-1jk} + \psi_{ijk}) S^i_{-\frac{1}{2}jk}$$

(10)

\(^2\) The unit of vector potential, expressed in cgs units, is \(zmc^2/e\), where \(z\) is the fine structure constant, \(m\) is the electronic mass, \(c\) is the speed of light, and \(e\) is the electronic charge.
\[
F^\eta_{ij,k} = \left[ -\frac{i}{2} \psi_{ijk} - \psi_{ij-1,k} + \frac{A^\eta}{2} (\psi_{ij-1,k} + \psi_{ij,k}) \right] S^\eta_{ij,k}
\]

(11)

\[
F^\epsilon_{ij,k} = \left[ -\frac{i}{2} \psi_{ijk} - \psi_{ij,k-1} + \frac{A^\epsilon}{2} (\psi_{ij,k-1} + \psi_{ij,k}) \right] S^\epsilon_{ij,k}
\]

(12)

Here, the scale factors and vector potential components are understood to be evaluated at the center of the appropriate cell wall. Finally, the finite volume discretization of the TDSE can be written as

\[
V_{ijk} \left( \partial_t - i \gamma_{ijk} \right) \psi_{ijk} = F^\eta_{ij-1,k} - F^\epsilon_{ij+1,k} + F^\eta_{ij+1,k} + F^\eta_{ij-1,k} - F^\epsilon_{ij+1,k} - F^\epsilon_{ij-1,k}
\]

(13)

3. Temporal discretization

The wavefunction is advanced through a discrete time interval \( \Delta t \) by computing \( \tilde{U}(\Delta t)\psi \). Due to the fact that this requires an inversion of the Hamiltonian, updating \( \psi \) in a single multi-dimensional advance is rather difficult. However, the technique of operator splitting [7] can be used to reduce the multi-dimensional advance to a sequence of one-dimensional advances. This is advantageous because in one dimension, the spatial differencing operator is a tridiagonal matrix which can be efficiently inverted.

Operator splitting of Eq. (13) leads to a sequence of one dimensional problems

\[
V_i \left( \partial_t - \frac{i}{D} \chi_i \right) \psi_i = F_{i-1} - F_{i+1}
\]

(14)

where \( D \) is the number of spatial dimensions in the overall problem, and the subscripts and superscripts relating to the ignored coordinates are suppressed. Using a superscript to indicate the time level, the Cayley form is arrived at by making the substitutions \( \partial_t \psi_i \to (\psi_i^{n+1} - \psi_i^n)/\Delta t \), and \( q_i \to q_i^0/2 + q_i^{n+1}/2 \), where \( n \) is the time level at the start of the step, and \( q \) represents any of the quantities \( \chi, \psi \), or \( F \). This gives the matrix equation

\[
\left( 1 + \frac{1}{2}iH\Delta t \right) \psi_i^{n+1} = \left( 1 - \frac{1}{2}iH\Delta t \right) \psi_i^n
\]

(15)

where the non-zero elements of the matrix \( H \) are

\[
H_{i-1} = \frac{S_{i-1/2}}{2V_i} \left( -\frac{1}{\Lambda_{i-1/2}} + iA_{i-1/2} \right)
\]

(16)

\[
H_{i+1} = \frac{S_{i+1/2}}{2V_i} \left( \frac{1}{\Lambda_{i+1/2}} + iA_{i+1/2} \right) + \frac{S_{i+1/2}}{2V_i} \left( \frac{1}{\Lambda_{i+1/2}} - iA_{i-1/2} \right) \frac{X_i^{n+1}}{D}
\]

(17)

\[
H_{i-1} = \frac{S_{i-1/2}}{2V_{i-1}} \left( -\frac{1}{\Lambda_{i-1/2}} - iA_{i-1/2} \right)
\]

(18)

and \( \Lambda_{i\pm 1/2} = \Lambda_i (\xi_i - \xi_{i\pm 1}) \). Note that the matrix \( H \) is not Hermitian unless \( V_i = V_{i+1} \). This comes about because in a general coordinate system, \( H \) is not the true Hamiltonian matrix. It is, however, related to the Hamiltonian matrix by a similarity transformation. In the following, it is shown that the Hamiltonian matrix derived from \( H \) is always Hermitian, and that this is sufficient to guarantee conservation of probability.

4. Conservation of probability

In Dirac notation, conservation of probability is expressed by \( \partial_t \langle \psi | \psi \rangle = 0 \). In order to discretize this, it is useful to define a diagonal matrix

\[
A_{ii} = \sqrt{V_i}
\]

(19)

Then the correspondence between a Dirac bracket and its discrete analogue is

\[
\langle \psi | \phi \rangle \rightarrow \psi^\dagger A \phi
\]

(20)

The discrete analogue of the time translation operator \( \tilde{U} \) is the matrix

\[
U = \frac{1 - \frac{1}{2}iH\Delta t}{1 + \frac{1}{2}iH\Delta t}
\]

(21)
Hence, conservation of probability for the discrete system is expressed as

\[ (\mathcal{U}\psi)^\dagger A^i A (\mathcal{U}\psi) = \psi^\dagger A^i A \psi \]  

(22)

A simple manipulation shows that this will hold provided \(UU^\dagger = 1\), where

\[ U = AA^{-1} \]  

(23)

In other words, it is the “weighted” matrix, \(U\), rather than the “bare” matrix, \(\mathcal{U}\), that must be unitary.

The Hamiltonian matrix elements for a bounded continuous system are determined by the bracket

\[ \hat{H}_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle \]  

(24)

where \(\{\phi_i\}\) is some set of basis functions. In the discrete space, one may define the position basis as those vectors \(\{b_i\}\) that have a non-zero element only in the \(i\)th position. The value of the non-zero element is determined from the orthonormality condition

\[ b^\dagger_i A^j b_j = \delta_{ij} \]  

(25)

where \(\delta_{ij}\) is the Kronecker delta function. Using this basis, and using the correspondence (20) to find the discrete analogue of (24), gives the Hamiltonian matrix of the discrete system as

\[ \hat{H} = AA^{-1} \]  

(26)

It then follows that

\[ U = \frac{1 - \frac{i}{2} \mathcal{H} \Delta t}{1 + \frac{i}{2} \mathcal{H} \Delta t} \]  

(27)

Clearly, \(U\) is unitary provided \(\mathcal{H}\) is Hermitian. But the effect of the similarity transformation \(AA^{-1}\) is just to multiply \(H_{ij}\) by \(\frac{\sqrt{V_i/V_j}}{\sqrt{V_i/V_j}}\). The Hamiltonian matrix is therefore

\[ H_{i-1,i} = \frac{S_i}{2\sqrt{V_iV_{i-1}}} \left( -\frac{1}{\Lambda_i} + i \Lambda_i \right) \]  

(28)

\[ H_{ii} = \frac{S_i}{2V_i} \left( \frac{1}{\Lambda_i} + i \Lambda_i \right) + \frac{S_{i+1}}{2V_i} \left( \frac{1}{\Lambda_{i+1}} - i \Lambda_{i+1} \right) - \frac{n^2}{D} \]  

(29)

\[ H_{i-1,i} = \frac{S_i}{2\sqrt{V_iV_{i-1}}} \left( -\frac{1}{\Lambda_i} - i \Lambda_i \right) \]  

(30)

which is clearly Hermitian. Thus, the Cayley form of the time translation operator guarantees conservation of probability on an arbitrary structured grid, provided the spatial discretization is carried out using finite volumes.

5. Phase accuracy

The phase accuracy of the time translation matrix \(\mathcal{U}\) can be analyzed in the case where \(\mathcal{H}\) is independent of time and the numerical grid is one dimensional (it need not be Cartesian). The phase error is due to spatial and temporal discretization errors. By expanding the discrete wavefunction in terms of the eigenvectors of \(\mathcal{H}\), it can be shown that

\[ \mathcal{U}\psi = \sum_i \exp \left[ i \tan^{-1} \left( \frac{-E_i \Delta t}{1 - \frac{i}{2} E_i^2 \Delta t^2} \right) \right] C_i \phi_i \]  

(31)

where \(\{\phi_i, E_i\}\) are the eigenvector-eigenvalue pairs, and \(C_i\) are the expansion coefficients. Expanding the inverse tangent to third order in \(\Delta t\) gives

\[ \mathcal{U}\psi = \sum_i e^{-i(1 - \epsilon_i) E_i \Delta t} C_i \phi_i \]  

(32)

where

\[ \epsilon_i = \frac{E_i^2 \Delta t^2}{12} \]  

(33)

The spatial discretization error enters the phase evolution through the eigenvalues \(E_i\), which differ from the eigenvalues of the true Hamiltonian, \(\hat{H}\). The temporal discretization causes a downshift in the apparent energy of each eigenmode by the...
fractional amount, $\epsilon$. These errors, as well as those arising in more complex cases, are discussed further in the section on numerical experiments.

6. Remarks on implementation

The implementation of the preceding discretization scheme has three basic elements: an eigensolver to compute the initial wavefunction, a tridiagonal inversion to compute $U\psi$, and a means of parallelizing the calculation.

To initialize the problem, one typically wants to start with a stationary state consistent with some prescribed potential, $\Phi$. This means solving the eigensystem $\mathcal{H}\phi_i = E_i\phi_i$, where $E_i$ is an energy eigenvalue. In multi-dimensions, this can be a substantial problem in its own right. However, if the initial state is spherically symmetric, the problem can be initialized by calculating the initial wavefunction on an auxiliary one dimensional spherical grid, and resampling the resulting data on whatever grid is used to model the time evolution. The solution of the eigensystem on the auxiliary grid can be facilitated by solving the weighted problem $H\phi'_i = E_i\phi'_i$, where $\phi'_i = A\phi_i$. This is advantageous since $H$ is real and symmetric (assuming $A = 0$ at $t = 0$), and can therefore be diagonalized efficiently. Since $\mathcal{H}$ and $H$ are related by a similarity transformation, both matrices have the same eigenvalues.

To advance the wavefunction in time, $U\psi$ has to be calculated for each one dimensional slice of the three dimensional array $\psi_{\theta r}$. This involves a sequence of tridiagonal inversions. Preparing the tridiagonal matrix $\mathcal{H}$ is a matter of specifying a grid geometry, and computing the associated cell volumes, wall areas, and scale factors. Also, the spatial dependence of the components of $A$ may have to be computed.

Parallelization might be accomplished in a variety of ways. In our work we use three dimensional domain decomposition. The tridiagonal inversions are decomposed across domains using the scheme described in Ref. [8]. This parallelization scheme results in an overhead of roughly a factor of three because of the fact that the matrix being inverted depends on time (the vectors $v$ and $w$ from Ref. [8] have to be computed every time level). However, it requires very little message passing compared to the transpose technique, and scales particularly well in multi-dimensions.

In the implementation of any numerical scheme for solving the TDSE, it is useful to have the option of making a transformation

$$\tilde{\psi} = \psi \exp \left( \frac{i}{\hbar} \int_0^t A(t')^2 dt' \right) \tag{34}$$

The new wavefunction, $\tilde{\psi}$, evolves according to a new Hamiltonian, which is obtained from the old one by making the substitution $\chi \to \Phi$. In other words, the transformation (34) causes the $A^2$ term to drop out of the TDSE. In some cases, this modifies the spectrum of the wavefunction such that the problem under consideration can be modeled using fewer time steps. However, the transformed problem has peculiar characteristics, such as negative frequencies even when $\Phi = 0$. On the other hand, any observable in the old representation may be applied to $\tilde{\psi}$ just as well as to $\psi$, for these differ only by a global phase factor. For example, the old Hamiltonian may be used with $\tilde{\psi}$ to obtain the true spectrum (cf. Ref. [9–11]). In the examples considered below, the transformation (34) is not used.

Another transformation that is sometimes used is to multiply the wavefunction by a geometric weighting factor. For example, using spherical coordinates, many authors make the transformation $\psi \to r\psi$, so that the state vector vanishes at $r = 0$. This procedure is unnecessary when using finite volumes. The transformed wavefunction is the same as $A\psi$, to within a constant factor. Advancing $A\psi$ using $U$ is the same as advancing $\psi$ using $U$, to within a round-off error.

7. Numerical experiments

In order to demonstrate the capabilities of the code we developed based upon the preceding concepts, three numerical experiments are carried out. First, a discrete approximation to the ground state of hydrogen is initialized on a spherical grid, and is evolved in time. This serves as a basic check on the conservation properties of the scheme, as well as its phase accuracy. Second, a quasi-classical wave packet is initialized on a Cartesian grid, and is subjected to an electromagnetic field. The results are compared with the analytical quasi-classical solution, i.e., the Volkov wavefunction. Finally, photoionization of hydrogen is modeled on a cylindrical grid, and the results are compared with tunneling theory.

7.1. Hydrogen atom

In order to model the ground state of hydrogen, it is most efficient to use spherical coordinates $(r, \theta, \phi)$, since only $r$ has to be resolved. Due to the finite resolution of the grid, the potential $\Phi$ cannot be a perfect Coulomb potential. Instead, we use the soft core potential

$$\Phi = \frac{1}{\sqrt{r_0^2 + r^2}} \tag{35}$$

where for the present example $r_0 = 0.01$. This potential is discretized on a radial grid with $2^{14}$ cells of width $\Delta r = 0.01$. The ground state energy associated with the matrix $\mathcal{H}$ is then (to six figures) $E_0 = -0.499416$. The eigenvector $\psi_0$ associated with
$E_0$ is initialized on the grid and advanced through 2500 steps with $\Delta t = 0.2$. Fig. 1 shows the results of the calculation. The curve plotted in Fig. 1(a) shows that probability is conserved to 12 digits after the round-off error accumulates for 500 a.u. The phase error is illustrated in Fig. 1(b), where the simulated phase is compared with the exact phase of hydrogen, $\arg \exp(i \frac{t}{2})$, as well as the phase that would be developed in the limit of vanishing time step, $\arg \exp(-i E_0 t)$. The dotted curve is the exact phase of hydrogen, the dashed curve is the vanishing time step phase, and the solid curve is the actual simulated phase. The difference between the dotted and dashed curves measures the spatial discretization error, which after 500 a.u. is about 0.29 radians. The difference between the dashed and solid curves measures the temporal discretization error, which after 500 a.u. is about 0.21 radians. This is exactly as predicted by Eq. (32). It should be noted that although the phase error accumulates, the instantaneous frequency is accurate to 0.1% at all times.

### 7.2. Volkov state

The wavefunction of an electron in a uniform electromagnetic field can be expanded in terms of Volkov states. The Volkov wavefunction with canonical momentum $P$, in the non-relativistic limit, is $\psi_V = e^{iS}$, where to within an additive constant

$$S = P \cdot r - \frac{1}{2} \int_0^t dt' [P + A(t')]^2$$

(36)

Here, $P$ is a constant. Strictly, $\psi_V$ extends over all space, and therefore cannot be simulated on any finite grid. However, a wave packet of the form

$$\psi_{wp} = C_n e^{-r^2/\sigma^2} e^{-y^2/\sigma^2} e^{iS}$$

(37)

is an approximate solution of the TDSE provided the quasi-classical condition, $\sigma \gg 2\pi/P$, is satisfied. In the present example, $\sigma = 1500$. $P = -0.4 (e_x + e_y)$, and $C_n$ is a normalization constant. The canonical momentum $P$ is chosen to make an angle of $\pi/4$ with respect to the grid lines in order to maximally stress the accuracy of the operator splitting technique. The vector potential is

$$A = -A_0 \frac{\omega_0}{2\sqrt{2}} (1 - \cos (\omega_0 t)) (e_x + e_y)$$

(38)

where $A_0 = 0.2$, and $\omega_0 = 0.057$. This form assures that both $A$ and $\partial_t A$ vanish at $t = 0$.

The cell sizes and time step must be chosen to resolve the highest wavenumbers and frequencies that occur in the Volkov state being modeled. The conditions on the cell sizes are $\Delta x \ll 2\pi/P_x$ and $\Delta y \ll 2\pi/P_y$. The condition on the time step is

$$\Delta t \ll \frac{2\pi}{\max{|\partial_t S|}}$$

(39)

where “max” selects the peak value of its argument. For the present example, these inequalities are satisfied by $\Delta x = \Delta y = 0.5$ and $\Delta t = 1.0$. The dimension of the grid is $2^{15} \times 2^{15}$, which is sufficient to prevent interactions with the boundary. The wave packet is initialized on the grid at $t = 0$, and is allowed to evolve for 500 a.u. The accuracy of the calculation is illustrated in Fig. 2. Fig. 2(a) shows that probability is conserved to 14 digits after 500 a.u. Fig. 2(b) shows that the simulated phase accurately tracks the phase of the Volkov wavefunction, $S$. If the phase error is plotted vs. time, one finds that it has a
part that grows linearly, and a part that oscillates. The phase error at $t = 500$ a.u. is about $0.048$ radians. As before, it should be noted that although phase errors grow in time, errors in the instantaneous frequency do not.

### 7.3. Tunneling ionization

The theory of tunneling ionization is well developed [12–17]. Although tunneling theories have been benchmarked against experiments with some success [18,19], comparisons with full scale, first principles simulations appear to be lacking. One reason for this may be that the computation time increases as one moves from the multiphoton regime to the tunneling regime (see below). In this section, a parameter regime where tunneling theory agrees with full scale simulations is identified.

Consider tunneling ionization of a hydrogen atom in the ground state by a field of the form $A = \frac{1}{2} A_0 [1 - \cos(\omega_0 t)] e_z$. Then, the $z$-axis is an axis of rotational symmetry, and the problem can be solved in two dimensions using any coordinate system with the same symmetry (e.g., cylindrical, parabolic, etc). In the present example, the cylindrical coordinates $(\rho, \phi, z)$ are used. This choice is suggested by the fact that the Volkov states for $z$-polarized radiation have phase fronts that line up with constant $z$ planes.

The parameters $A_0$ and $\omega_0$ are chosen to satisfy the assumptions of tunneling theory as closely as possible. In the case of hydrogen, the assumptions are $\omega_0 \ll 1/2$, $\nu \ll 1$, and $|\mathcal{E}| \ll 1$, where $\nu$ is the adiabaticity parameter [12], and $\mathcal{E}$ is the electric field. For the form of the field considered here, $\nu = 2/A_0$ and $|\mathcal{E}| = -e \omega_0 A_0 \sin(\omega_0 t)/2$. If the above conditions are satisfied, the rate of tunneling for the hydrogen atom is [20]

$$W_H(t) = \frac{4}{|\mathcal{E}(t)|^2} \exp \left( -\frac{2}{3|\mathcal{E}(t)|} \right)$$

A refinement of this is [21]

$$W_5(t) = \frac{4}{|\mathcal{E}(t)|} (2U(t))^{5/2} \exp \left( -\frac{2(2U(t))^{3/2}}{3|\mathcal{E}(t)|} \right)$$

where $U(t) = U(|\mathcal{E}(t)|)$ is the Stark shifted ionization potential [22]. Choosing $A_0 = 10$ and $\omega_0 = 0.01$, and integrating $W_H(t)$ over one half-cycle of the radiation field, gives $\sim 1\%$ for the probability of ionization.

In order to compute the numerical ionization rate, the probability of finding an electron far from the atom is differentiated with respect to time. In particular,

$$W(t) = -\partial_t \int_B \frac{1}{8} \mathbf{r} \cdot \mathbf{r} \left| \psi(t) \right|^2$$

where $B$ is any spherical region centered on the atom with radius $R \gg 1$. Discretizing the integration allows comparison of the simulated rate, $W(t)$, with the theoretical rate, $W_H(t)$.

The discretization parameters of the simulation have to satisfy conditions arising from both Volkov states and bound states. The requirements arising from bound states are that the lowest several bound state energies should be close to those of hydrogen, and that the frequency of the ground state should be well resolved. The condition on the time step is $\Delta t \ll 4\pi$. The requirement on the space step is determined by computing the eigenvalues of $\mathcal{H}$ on various spherical grids until the bound state energies match those of hydrogen to the desired accuracy. If one chooses a grid with $2^{12}$ cells and $\Delta r = 0.02$,
and a soft core potential with \( r_a = 0.025 \), the bound state energies are as shown in Table 1. For these parameters, there are seven bound states. The first six states have energies that correspond very accurately to the energy levels of hydrogen. As discussed above, the time dependent problem is initialized by computing the ground state wavefunction on the auxiliary spherical grid, and resampling it on the cylindrical grid used for the time advance. Because of the resampling, the initial state is stationary only to within a discretization error. This leads to a small overlap of the initial state with excited states and free states even before any field is applied. Therefore, the ionization rate under study must be large enough to overwhelm the associated errors.

The discretization requirements arising from Volkov states are given in Section 7.2. To apply the requirements, one needs to know the momentum spectrum that develops during the tunneling ionization process. An estimate is obtained by assuming that the mechanical momentum is negligible at the time the Volkov wave packet is emitted. Assuming the wave packet is emitted at the peak of the electric field, this gives \( P = -\frac{1}{2}A_{0}\rho \mathbf{e} \), and \( \max |\langle \partial_{\rho} S \rangle| = \frac{1}{2}A_{0}^{2} \).

The results from three simulations with different values of \( \omega_{0} \) are shown in Fig. 3. The grid dimensions are \( N_{x} \times N_{z} = 2^{12} \times 2^{15} \), with \( \Delta \rho = \Delta z = 0.02 \). The large number of z-cells prevents waves from interacting with the simulation boundary. The time step is \( \Delta t = 0.01 \), the peak vector potential is \( A_{0} = 10 \), and the diagnostic sphere has radius \( R = 10 \). Fig. 3 compares the simulated rate, \( W(t) \), with the theoretical rates, \( W_{H}(t) \) and \( W_{S}(t) \), for the cases \( \omega_{0} = 0.008 \), \( \omega_{0} = 0.010 \), and \( \omega_{0} = 0.012 \). The disparity between theory and simulation increases with increasing \( \omega_{0} \). This is presumably due to the condition \( |\xi| \ll 1 \), which in the present case corresponds to \( \omega_{0} \ll 0.2 \). Although this condition seems to be well satisfied, a closer study of the theory shows that a more complete statement of the condition is \( 1 \ll \eta_{0} \ll 1/|\xi| \), where \( \eta_{0} \) is a parameter characterizing the distance from the origin to the quasi-classical region [20]. This condition is stronger than \( |\xi| \ll 1 \). Further sources of disparity are the imperfect fulfillment of the adiabaticity condition \( (A_{0} \gg 2) \), and the re-sampling error in the numerical ground state. We believe this last effect is responsible for the oscillatory features in Fig. 3(a).

The ionization rate measures the flux of a wave packet through a diagnostic sphere with radius \( R \). Due to the fact that any wave packet spreads as it propagates, the choice of \( R \) affects the ionization rate. This is illustrated in Fig. 4 for the cases \( R = 10 \), \( R = 30 \), and \( R = 100 \). The parameters are the same as those of Fig. 3, except that only the case where \( \omega_{0} = 0.012 \) is shown. Fig. 4(a) shows that the peak ionization rate diminishes as the radius of the diagnostic sphere increases. This is because as the wave packet spreads, the peak value of \(|\psi|^{2}\) has to decrease, assuming the total probability in the wave packet is conserved. The conservation of total probability in the wave packet is demonstrated in Fig. 4(b). The time delay associated

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</tbody>
</table>

Fig. 3. Ionization rate as a function of time for hydrogen during about one half-cycle of the radiation field. The peak vector potential is \( A_{0} = 10 \). Panel (a) is for \( \omega_{0} = 0.008 \), (b) is for \( \omega_{0} = 0.010 \), and (c) is for \( \omega_{0} = 0.012 \).
with $R$ reflects the finite propagation speed of the wave packet. Presumably, the “best” value of $R$ is the distance between the atom and the location where electrons are detected.

7.4. Parallel scaling

Finally, the scaling characteristics of the calculation are shown in Fig. 5. The parameters of the calculation were exactly those used in the tunneling calculation, except that the problem was only run for 100 time steps. The scaling study was done on the Cray XT4 “Franklin” at the National Research Energy Scientific Computing Center (NERSC). The calculation was run as a pure Message Passing Interface (MPI) calculation. The domain decompositions used were $16 \times 16$, $16 \times 32$, $16 \times 64$, $16 \times 128$, $32 \times 128$, and $64 \times 128$, where the first number is the number of $\rho$-domains and the second is the number of $z$-domains. The problem exhibits strong scaling (wall clock time is halved when the number of cores is doubled) for up to $2^{12}$ cores. This result is about as expected. The parallelization scheme works best when the number of domains in a given direction is much smaller than the number of cells per domain in the same direction. This condition is violated for $2^{12}$ processor cores.

8. Conclusion

An efficient, strictly conservative, parallel algorithm for solving the TDSE on an arbitrary structured grid may be formulated based on finite volumes. The numerical computation requires calculation of the volumes of the cells and the areas of the cell walls, which are in turn used to construct a matrix $\mathcal{H}$, which is related to the Hamiltonian matrix by a similarity transformation. When the wavefunction is advanced in time using the Cayley form of $\exp(-i\mathcal{H} \Delta t)$, strict conservation of probability results, no matter what the grid geometry. In one dimension, the time advance is carried out by solving a tridiagonal matrix equation. Extension to multi-dimensions is achieved via straightforward operator splitting. The phase
accuracy of the algorithm is third order in the time step, and two dimensional photoionization problems can be scaled to thousands of processor cores.

Acknowledgements

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Appendix A. Finite volume parameters

In this appendix, tables are given with the finite volume parameters for cylindrical, spherical, and parabolic coordinates. The primary finite volume parameters are the cell volume, \( V \), and the three wall areas, \( S_r \), \( S_\theta \), and \( S_z \). The accuracy of conservation of probability is only as good as the accuracy of these parameters. In order to construct the matrix \( \mathcal{M} \), one also needs the scale factors, \( h_r \), \( h_\theta \), and \( h_z \), and the components of the vector potential in terms of the curvilinear coordinates. Since it is usually the Cartesian components that are known at the outset, it is useful to have a matrix \( T^{-1} \), which transforms Cartesian components into curvilinear components. The matrix \( T \) is orthogonal, so its inverse is its transpose.

The cylindrical coordinates are defined by \( x = \rho \cos \varphi \), \( y = \rho \sin \varphi \), and \( z = z \). The corresponding finite volume parameters are given in Table 2. The spherical coordinates are defined by \( x = r \sin \theta \cos \varphi \), \( y = r \sin \theta \sin \varphi \), and \( z = r \cos \theta \). The corresponding finite volume parameters are given in Table 3. The parabolic coordinates are defined by \( x = \sqrt{\xi \eta} \cos \varphi \), \( y = \sqrt{\xi \eta} \sin \varphi \), and \( z = (\xi - \eta)/2 \). The corresponding finite volume parameters are given in Table 4.

In the tables, coordinates appear with an integer subscript 0, 1, or 2. The subscript 0 indicates evaluation at the cell center, 1 indicates evaluation at the lower cell wall, and 2 indicates evaluation at the upper cell wall. A coordinate prefixed with \( \xi \) or \( \eta \) is shorthand for the difference \( \xi_2 - \xi_1 \) or \( \eta_2 - \eta_1 \).

The formula given in the text was based on an approximation of arc length. For example, the approximation

\[ \int_{\xi_1}^{\xi_2} d\xi h_\xi \approx (\xi_2 - \xi_1) h_\xi(\xi_0) \]  

was used. While this is exact for cylindrical or spherical coordinates, it is approximate for parabolic coordinates.

### Table 2

Finite volume parameters in cylindrical coordinates.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scale factor, ( h_r )</td>
<td>1</td>
</tr>
<tr>
<td>Scale factor, ( h_\theta )</td>
<td>( \rho )</td>
</tr>
<tr>
<td>Scale factor, ( h_z )</td>
<td>1</td>
</tr>
<tr>
<td>Radial length, ( r )</td>
<td>( \sqrt{\rho^2 + z^2} )</td>
</tr>
<tr>
<td>Cell volume, ( V )</td>
<td>( \rho_0 \rho \Delta \rho \Delta \varphi )</td>
</tr>
<tr>
<td>Wall area, ( S_r )</td>
<td>( \rho \Delta \rho \Delta z )</td>
</tr>
<tr>
<td>Wall area, ( S_\theta )</td>
<td>( \Delta \rho \Delta z )</td>
</tr>
<tr>
<td>Wall area, ( S_z )</td>
<td>( \frac{1}{2} \Delta \rho(\rho_2^2 - \rho_1^2) )</td>
</tr>
</tbody>
</table>

### Table 3

Finite volume parameters in spherical coordinates.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scale factor, ( h_r )</td>
<td>1</td>
</tr>
<tr>
<td>Scale factor, ( h_\theta )</td>
<td>( r )</td>
</tr>
<tr>
<td>Scale factor, ( h_\varphi )</td>
<td>( r \sin \theta )</td>
</tr>
<tr>
<td>Radial length, ( r )</td>
<td>( r )</td>
</tr>
<tr>
<td>Cell volume, ( V )</td>
<td>( \Delta \rho \Delta \varphi \left( \frac{2 \pi}{r^2} + 2r z \right) \sin \frac{\pi}{2} \sin \theta_0 )</td>
</tr>
<tr>
<td>Wall area, ( S_r )</td>
<td>( r^2 \Delta \varphi (\cos \theta_1 - \cos \theta_2) )</td>
</tr>
<tr>
<td>Wall area, ( S_\theta )</td>
<td>( \frac{1}{2} \Delta \theta (r_2^2 - r_1^2) )</td>
</tr>
<tr>
<td>Wall area, ( S_\varphi )</td>
<td>( \frac{1}{2} \Delta \theta (r_2^2 - r_1^2) )</td>
</tr>
</tbody>
</table>

### Table 4

Finite volume parameters in parabolic coordinates.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scale factor, ( h_r )</td>
<td>1</td>
</tr>
<tr>
<td>Scale factor, ( h_\theta )</td>
<td>( r )</td>
</tr>
<tr>
<td>Scale factor, ( h_\varphi )</td>
<td>( r \sin \theta )</td>
</tr>
<tr>
<td>Radial length, ( r )</td>
<td>( r )</td>
</tr>
<tr>
<td>Cell volume, ( V )</td>
<td>( \Delta \rho \Delta \varphi \left( \frac{\pi}{r^2} + 2r z \right) \sin \frac{\pi}{2} \sin \theta_0 )</td>
</tr>
<tr>
<td>Wall area, ( S_r )</td>
<td>( r^2 \Delta \varphi (\cos \theta_1 - \cos \theta_2) )</td>
</tr>
<tr>
<td>Wall area, ( S_\theta )</td>
<td>( \frac{1}{2} \Delta \theta (r_2^2 - r_1^2) )</td>
</tr>
<tr>
<td>Wall area, ( S_\varphi )</td>
<td>( \frac{1}{2} \Delta \theta (r_2^2 - r_1^2) )</td>
</tr>
</tbody>
</table>

Transformation of a vector, \( T \)

\[
\begin{pmatrix}
\cos \varphi \sin \theta & \cos \varphi \cos \theta & -\sin \varphi \\
\sin \varphi \sin \theta & \sin \varphi \cos \theta & \cos \varphi \\
\cos \theta & -\sin \theta & 0
\end{pmatrix}
\]
Table 4

Finite volume parameters in parabolic coordinates.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scale factor, ( b_z )</td>
<td>( \sqrt{\frac{2}{\pi}} )</td>
</tr>
<tr>
<td>Scale factor, ( b_\theta )</td>
<td>( \sqrt{\frac{2}{\pi}} )</td>
</tr>
<tr>
<td>Scale factor, ( b_\phi )</td>
<td>( \sqrt{\frac{2}{\pi}} )</td>
</tr>
<tr>
<td>Radial length, ( r )</td>
<td>( \frac{1}{2} (\xi + \eta) )</td>
</tr>
<tr>
<td>Cell volume, ( V )</td>
<td>( \frac{1}{4} \Delta \xi \Delta \eta \Delta \phi (\xi_0 + \eta_0) )</td>
</tr>
<tr>
<td>Wall area, ( S_z )</td>
<td>( \frac{1}{2} \Delta \phi \sqrt{\xi \left( \eta_1 + \frac{3}{2} \right)} )</td>
</tr>
<tr>
<td>Wall area, ( S_\theta )</td>
<td>( \frac{1}{2} \Delta \phi \sqrt{\eta \left( \xi_1 + \frac{3}{2} \right)} )</td>
</tr>
<tr>
<td>Wall area, ( S_\phi )</td>
<td>( \frac{1}{2} \left( \sqrt{\xi_2} - \sqrt{\xi_1} \right) \left( \sqrt{\eta_2} - \sqrt{\eta_1} \right) \left( \sqrt{\xi_1} + \sqrt{\xi_2} \right)^2 + \left( \sqrt{\eta_1} + \sqrt{\eta_2} \right)^2 )</td>
</tr>
</tbody>
</table>

References