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<https://escholarship.org/uc/item/3f80p718>

Journal

Journal of Chemical Theory and Computation, 21(24)

ISSN

1549-9618

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Publication Date

2025-12-23

DOI

10.1021/acs.jctc.5c01345

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Overset-Grid Method with Smooth Orbital Partitioning for Molecular Scattering Calculations

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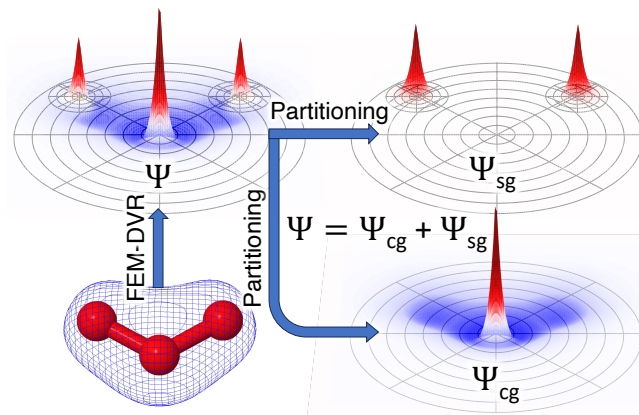
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Abstract

To solve molecular photoionization and electron scattering problems, we use an overset-grid representation of electronic continuum functions which has an extended central spherical grid that overlaps small spherical grids (subgrids) centered on each atom of a polyatomic molecule. Here we present an improved algorithm that smoothly partitions the total wave function between the central grid and the atomic subgrids. The smooth partitioning allows one to use approximately one fourth the number of partial waves on the central grid compared to our previous implementation with switching functions. The resulting numerical method for treating electron scattering and photoionization of polyatomic molecules combines the accuracy and flexibility of pure numerical grid representations with the rapid convergence of hybrid combinations of atom-centered basis-set expansions and grid methods. The overset-grid representation is implemented using the complex Kohn variational principle for scattering and photoionization amplitudes. The faster convergence with respect to number of central grid partial waves is demonstrated and accuracy verified by comparisons with the previous implementation and with far more computationally demanding single-center numerical expansions in electron-molecule scat-

tering and photoionization calculations on the neon dimer (Ne_2) system, carbon tetrafluoride (CF_4) molecule, and the pyridine ($\text{C}_5\text{H}_5\text{N}$) molecule in the static-exchange approximation.



1 Introduction

We recently introduced a computational approach to electron scattering and photoionization of polyatomic molecules based on overlapping three-dimensional numerical grids, called the overset-grid method^{1,2} that employs those grids in the complex Kohn scattering variational principle.³⁻⁶ Here we eliminate a limitation of the original approach that impeded

its application to coupled electronic channels with an idea that addresses a core problem that challenges all existing computational approaches to electron-molecule collisions. This problem is that in scattering calculations the relatively simple angular, but highly oscillatory radial behavior of the continuum wave function at large distances must be treated at the same time as its much more non-spherical behavior close to and inside the molecule itself.

Electron-molecule scattering and molecular photoionization are problems that continue to challenge accurate quantum mechanical calculation, and they have become more pressing problems to solve efficiently and accurately in the age of attosecond laser experiments. Attosecond optical pulses with durations of 150 attoseconds or shorter, which are common in modern ultrafast spectroscopy, have bandwidths comparable to the ionization energy of most small molecules, so experiments employing attosecond pulses almost always involve the photoionization continuum.

The target molecule can be left behind in both ground and electronically excited states, and thus the basic physics is a familiar but challenging multichannel scattering problem, complicated by the fact that the continuum electron is indistinguishable from those bound in the molecule. Although there are several successful and well-developed computational approaches for solving electron scattering problems, advances in ultrafast spectroscopic experiments compel us to seek more efficient and more general numerical algorithms that can also treat larger molecules. To improve on current approaches, we have to address the fundamental building block of those algorithms, namely the problem of electron-molecule scattering in which only a single target electronic state is considered.

Electron-scattering wave functions for small to medium-sized molecules at collision energies of chemical interest, i.e., less than about 50 eV, typically require relatively few angular momentum partial waves, $\ell_{\max} = 4$ to 15, to represent their asymptotic behavior at large distances from the molecule. However, the formally correct expansion of the complete scattering wave

function at all distances in partial waves around a single center converges extremely slowly and requires many hundreds or even thousands of spherical harmonics, because such an expansion poorly represents the wave function near the nuclei of a polyatomic molecule.

One successful approach to the electron-polyatomic molecule using the Schwinger variational principle uses highly optimized single-center expansions^{7,8} in the widely distributed code `ePolyScat`.⁹ Despite its drawbacks, there is a strong reason for such an approach. The single-center expansion approach allows for the use of flexible numerical grid representations of the scattering wave function in radial degrees of freedom.

Decleva and coworkers^{10,11} have implemented an approach for solving the scattering equations for continuum electronic states based on the use of multicenter B-spline basis sets. The multicenter B-spline method implicitly has a numerical overset grid when considering the knots in all radial intervals of the different centers. In contrast, the overset grid method proposed here uses an FEM-DVR basis on the central and subgrids. A more significant difference is that, as implemented in the `Tiresia` code,¹² the equations being solved are based on density functional theory, which for single-channel problems they use the Kohn-Sham (KS) equations with the PB94 exchange-correlation potential and for multi-channel problems they use the TDDFT extension of the KS formulation. Thus, compared to the exact non-local exchange potential used in our overset grid method, using the approximate semi-local PB94 potential simplifies the structure of the Hamiltonian so that the basis functions on different centers do not interact. No such approximations are made in the overset grid method we describe here. All nonlocal operators, like exchange operators and the free-particle Green's function, are treated in this numerical grid method with only numerical quadrature errors.

Such purely numerical grid methods, e.g., the B-spline^{13–15} or finite element discrete variable representation^{16–18} approaches have the distinct advantages that they can accurately treat the

oscillatory behavior of scattering wave functions at high energies and also can be adaptively converged by increasing the density of grid points.

All other methods solve this problem with various combinations of basis set expansions. For example, one might seek to expand the continuum wave function in the vicinity of the molecule in a multicenter Gaussian basis function expansion and combine that representation with a partial wave expansion asymptotically. The resulting technical difficulties have been solved in a variety of ways. One approach is the original complex Kohn variational method, which combines the Gaussian orbital description in the vicinity of the molecule that overlaps an additional basis of non-square integrable continuum functions, Bessel or Coulomb functions depending on the boundary conditions.^{3-6,19-24} Another approach is the popular and powerful *R*-matrix method which, generally speaking, effectively matches the two representations on the surface of a sphere containing the interaction region²⁵⁻²⁷ and has incorporated many refinements to this central idea in the UKRmol+ suite of codes,²⁸ notably including a B-spline basis set in the inner sphere to better represent the continuum functions. In recent years a new close-coupling method has been developed and implemented in a code called XCHEM, which also uses a hybrid basis of overlapping Gaussians and B-splines for molecular targets.²⁹⁻³¹ Yet another approach developed by Scrinzi and co-workers for molecular ionization employs a fully numerical finite element basis for the continuum combined with Gaussian basis expansions of molecular orbitals in a configuration interaction description of the target molecule,^{32,33} and also emphasizes the numerical advantages of the grid representation of the continuum.

The overset-grid method that we refine here makes a completely numerical description of the continuum portion of the wave function using small numerical grids centered on each atom that overlap a central grid that extends into the asymptotic scattering region as sketched in Figure 1. The full (*N*-electron) wave function is then expanded in antisymmetrized products

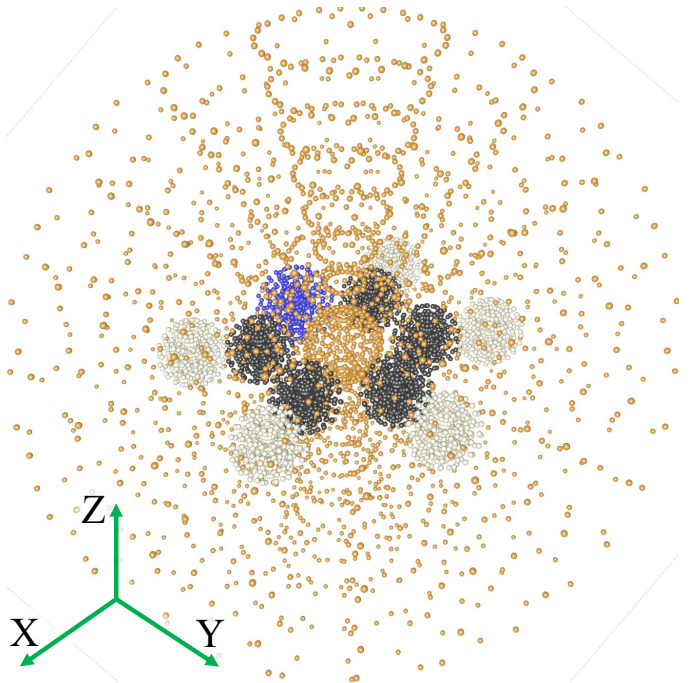


Figure 1: Schematic representation of the overset grid used in electron scattering and photoionization calculations for the pyridine molecule (C_5H_5N). The central grid (light brown) overlaps with several mutually non-overlapping spherical subgrids, each denser than the central grid in the sphere around each nucleus and radially adapted to the local momentum of the scattered electron. Subgrids are centered at off-center nuclei and correspond to different atomic types: hydrogen-equivalent subgrids (gray), carbon-equivalent subgrids (black), and the nitrogen subgrid (blue). Patch functions of low-order polynomials in each subgrid maintain continuity with a function on the central grid at the outer boundary of the subgrid.

of Gaussian orbitals describing target electrons and this grid representation of the one-electron continuum. This approach seeks to maximally exploit the advantages of grid methods, but solves the central problem of representing the continuum scattering orbitals both in the vicinity of the molecule and asymptotically in a new way.

In the next section, we explain the central idea of the overset-grid method and its new “patch-algorithm” modification that we are proposing here. Section 3 is devoted to

the brief description of the salient aspects of the complex Kohn variational approach to the electron-scattering problem and its implementation with the overset-grid method. We extensively test the patch algorithm and compare it to the original switching-function version for two scattering and two photoionization examples in Section 4. And finally, our conclusions are given in Section 5.

2 Overset-Grid Method with Patch Functions

The overset grid that describes a one-electron molecular continuum scattering wave function is illustrated in Figure 1 for the example of the pyridine (C_5H_5N) molecule. The grid consists of an extended central grid (centered in the middle of the six-membered ring in Figure 1) and eleven smaller but denser subgrids centered on each atom that do not overlap each other. All three-dimensional spherical grids are products of finite-element-method discrete-variable-representation (FEM-DVR) grids for the radial variable associated with each grid and a Gauss-Chebyshev and Gauss-Legendre quadrature in the angular variables.^{7,34} The basic idea is that the subgrids describe the wave function near each atom, and in particular any cusp behavior at the nuclei, whereas the central grid describes the wave function between the atoms and asymptotically.

We hasten to point out that the idea of overset grids is by no means original here; we are contributing only to its adaptation and the somewhat subtle aspects of its application to quantum wave functions, including the implementation of the operation of scattering Green’s functions. The overset-grid method is well-established in an extensive literature in various science and engineering disciplines that involve numerical simulation of systems with complex geometry, particularly in fluid dynamics and aerodynamics.^{35–39}

In our variant of the idea, the three-dimensional wave function, $\Psi(\mathbf{r})$, is described everywhere in space by its values at all the points on the grid. It is well-defined at each

stage of the scattering calculation, as we iteratively add more Born-Arnoldi numerical continuum basis functions to the calculation, as described in Section 3. At each stage, we represent $\Psi(\mathbf{r})$ on the overset grid and use that representation to calculate the results of the potential energy operator and the free-particle Green’s function operating on it.

Because the individual grids forming the overset grid overlap, we originally^{1,2} partitioned the wavefunction smoothly between them with Becke switching functions,⁴⁰ denoted by $W_g(\mathbf{r})$, associated with each grid g (either the central grid or the subgrids),

$$\Psi(\mathbf{r}) = \sum_g W_g(\mathbf{r})\Psi(\mathbf{r}) = \sum_g \Psi_g(\mathbf{r} - \mathbf{r}_{g,0}). \quad (1)$$

where $\mathbf{r}_{g,0}$ denotes the grid center. The switching functions rise smoothly across each subgrid boundary from zero outside to one inside the subgrid. The two sides of eq (1) are made equal by the condition that the switching functions sum globally to unity,

$$\sum_g W_g(\mathbf{r}) = 1. \quad (2)$$

On each grid separately (subgrids and central grid) we sought to efficiently expand the partitioned wave functions in the smallest necessary number of partial waves (radial functions times spherical harmonics, Y_{lm}),

$$\Psi_g(\mathbf{r}_g) = \sum_{lm}^{l_{g,\max}} \psi_{g,lm}(r_g)Y_{lm}(\Omega_g) \quad (3)$$

with $\mathbf{r}_g = \mathbf{r} - \mathbf{r}_{g,0}$. However, this seemingly optimum partitioning, which was used in our original implementation,^{1,2} suffers from a serious problem in the central grid.

The weight for the central grid must be the complement of all the subgrids, $W_{cg} = 1 - \sum_{sg} W_{sg}$, where sg denotes a subgrid and cg denotes the central grid. The central grid partitioned in this way has smooth edged holes in three dimensions, where each of the subgrids is effectively cut out of it. So, while the straightforward partitioning with Becke weights⁴⁰ al-

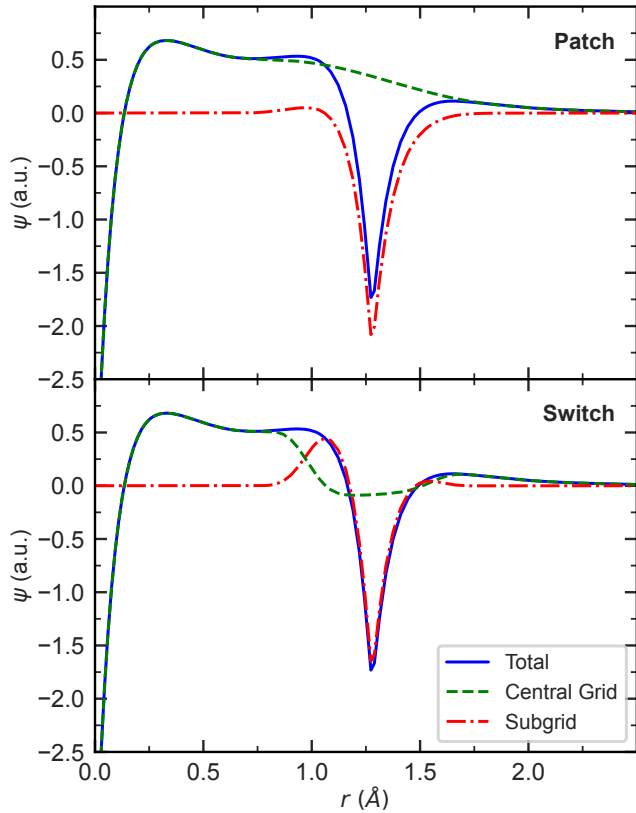


Figure 2: Details of the partitioning of the $3a_1$ orbital of O_3 plotted on a ray that passes from the central O atom through one of the terminal O atoms. In the upper panel the partition made by the patch algorithm (with $n = 3$ as defined in eq (7)) is shown and in the lower panel the corresponding switching-function partition is given. In both cases, the central grid and subgrid functions add to give the total function, which is the original orbital wave function

allows the use of very few partial waves (angular momenta) in the expansion of the wave function in each subgrid, the partial wave expansion in eq (3) for the wave function on the central grid must include enough partial waves to resolve the resulting “holes”. Despite the smooth edges of the holes that mirror the Becke switching functions W_{sg} , of the subgrids, the algorithm using switching functions required a maximum angular momentum for the central grid of at least $l_{g,\max} = 20$ or 30 , even in cases where the maximum necessary angular momentum in the asymptotic region was less than 10 .

Here, we develop a new variant of the overset-grid algorithm that repairs this deficiency. We

define the subgrids as before, non-overlapping but extending to nearly the middle of the shortest bond involving each atom. We eliminate the switching functions altogether in the representation of the wave function, and instead define a smooth “patch” in the central grid in three dimensions over each subgrid defined by its partial wave expansion within the subgrid. The figure in the abstract gives a notional picture for the ozone (O_3) molecule of how the cusps near the nuclei in a wave function are represented in the subgrids and not in the central grid. In Figure 2 one-dimensional cuts through the same orbital are given for both the patch algorithm and the original switching-function algorithm.^{1,2}

For a subgrid (sg) centered at a nucleus with radial coordinate r_{sg} we define a patch function $P_{sg}(\mathbf{r})$ by its expansion in partial waves:

$$P_{sg}(\mathbf{r}) = \sum_{lm}^{l_{sg,\max}} P_{sg,lm}(r_{sg}) Y_{lm}(\theta_{sg}, \phi_{sg}). \quad (4)$$

Recall that the radial points r_{sg} are FEM-DVR grid points, and the θ_{sg} and ϕ_{sg} points are angular quadrature points. The radial functions defining the patch, $P_{sg,lm}(r)$, are chosen to have the specific polynomial form:

$$P_{sg,lm}(r) = r^l \sum_{k=0}^{n-1} c_k r^{2k} \quad (5)$$

so that they satisfy the appropriate boundary condition at $r_{sg} = 0$, but have no derivative discontinuity at the center of the subgrid. The product $r^l Y_{l,m}$ has the property of being a harmonic polynomial,⁴¹ and has no slope discontinuities at the origin. Multiplying by an even polynomial in r maintains the continuity of the derivatives with respect to the Cartesian coordinates at the origin of the subgrids.

We determine the coefficients, c_k , in eq (5) for each partial-wave component of the patch functions by matching the value and a fixed number of derivatives with Ψ at the boundary of the subgrid. We define the radial functions of the expansion of $\Psi(\mathbf{r})$ on the subgrid by the projec-

tion on the spherical harmonics in the subgrid,

$$\varphi_{sg,lm}(r_{sg}) = \int_{S_{sg}} Y_{lm}^*(\Omega_{sg}) \Psi(\mathbf{r}) d\Omega_{sg} \quad (6)$$

where Ω_{sg} denotes θ_{sg}, ϕ_{sg} , $d\Omega_{sg} = \sin \theta_{sg} d\theta_{sg} d\phi_{sg}$, and the surface S_{sg} is defined by $r_{sg} = |\mathbf{r} - \mathbf{r}_{sg,0}|$. Then the n values of the c_k coefficients defining the polynomial patch are determined by the conditions,

$$\left. \frac{d^k P_{sg,lm}}{dr^k} \right|_{r=r_{sg,\max}} = \left. \frac{d^k \varphi_{sg,lm}}{dr^k} \right|_{r=r_{sg,\max}}, \quad (7)$$

$$k = 0, 1, \dots, n-1.$$

for each subgrid and where $r_{sg,\max}$ is the radius of the subgrid.

Now we define the part of the wave function partitioned onto each subgrid, $\Psi_{sg}(\mathbf{r}_{sg})$, as the *difference* between $\Psi(\mathbf{r})$ projected onto the small number of spherical harmonics associated with the subgrid and the patch function specified by the c_k coefficients in eq (5):

$$\Psi_{sg}(\mathbf{r}_{sg}) = \sum_{lm}^{l_{sg,\max}} \psi_{sg,lm}(r_{sg}) Y_{lm}(\Omega_{sg}), \quad (8)$$

$$\psi_{sg,lm}(r_{sg}) = \varphi_{sg,lm}(r_{sg}) - P_{sg,lm}(r_{sg}).$$

The $\Psi_{sg}(\mathbf{r}_{sg})$ functions are localized on the subgrids and capture the rapid variations in the wave functions induced by the presence of the nuclei at the center of the subgrids.

The central grid overlaps all the subgrids, which means that many points ($r_{cg}, \theta_{cg}, \phi_{cg}$) of the central grid (cg) lie inside the subgrids. Inside the subgrids, the central grid represents not only the patch function but the entire difference between Ψ_{sg} and Ψ , which includes the small error generated by limiting the angular momenta in the subgrid to $l \leq l_{sg,\max}$. To that end, we interpolate the subgrid functions $\Psi_{sg}(\mathbf{r})$ onto the central grid points that lie within the subgrid,

$$\Psi_{cg \leftarrow sg}(\mathbf{r}_{cg}) = \begin{cases} \Psi_{sg}(\mathbf{r}_{cg} - \mathbf{r}_{sg,0}) & |\mathbf{r}_{cg} - \mathbf{r}_{sg,0}| \leq r_{sg,\max} \\ 0 & \text{otherwise} \end{cases} \quad (9)$$

where we have used the fact that $\mathbf{r}_{cg} = \mathbf{r}$ since $\mathbf{r}_{cg,0} = 0$. The interpolation to a specific point $\mathbf{r}_{cg} - \mathbf{r}_{sg,0}$ from the values of $\Psi_{sg}(\mathbf{r}_{sg})$ defined on a set of subgrid points $\{\mathbf{r}_{i,sg} : i = 1, \dots, N_{sg}\}$, is accomplished, as explained by Greenman et al.,¹ using the interpolating polynomials of the subgrid FEM-DVR in the radial dimension, r_{sg} , and the analytically known spherical harmonics of the angles, θ_{sg} and ϕ_{sg} .

Then the wave function on the central grid is

$$\Psi_{cg}(\mathbf{r}_{cg}) = \Psi(\mathbf{r}_{cg}) - \sum_{sg} \Psi_{cg \leftarrow sg}(\mathbf{r}_{cg}). \quad (10)$$

The three relations, eqs (8), (9) and (10), complete the partitioned representation of the wave function, $\Psi(\mathbf{r})$, on the complete overset grid. This partitioning algorithm largely captures truncation errors in the subgrid representation of the full wave function, due to the limited number of partial waves used in each subgrid, through the subtraction in eq (10).

Effectively, for points on the central grid, $\mathbf{r}_{cg}$ that lie inside one of the subgrids, sg , the central-grid expansion represents the smooth patch plus the small truncation error, $\epsilon(\mathbf{r})$, from the limited partial-wave expansion of the wave function $\Psi(\mathbf{r})$ on the subgrid,

$$\Psi_{cg}(\mathbf{r}_{cg}) = \underbrace{\sum_{lm}^{l_{sg,\max}} P_{sg,lm}(|\mathbf{r}_{cg} - \mathbf{r}_{sg,0}|) Y_{lm}(\Omega_{\mathbf{r}_{cg} - \mathbf{r}_{sg,0}})}_{\text{patch}} + \underbrace{\epsilon(\mathbf{r}_{cg})}_{\substack{\text{Truncation error} \\ \text{from small} \\ \ell_{sg,\max} \text{ on sg}}} \quad \text{for } |\mathbf{r}_{cg} - \mathbf{r}_{sg,0}| \leq r_{sg,\max} \quad (11)$$

The figure in the abstract and Figure 2 illustrates the patching algorithm for the ozone (O_3) sigma-bonding $3a_1$ orbital, which is primarily composed of atomic 2s orbitals on each oxygen. The bond length from the central O atom to either of the terminal O atoms was 1.27 Å. This orbital is partitioned into two parts: the contribution of the middle oxygen that is expanded on the central grid, centered at the origin, while the contribution of the terminal oxygens whose electron density and cusp of the 2s orbital at

the nucleus is partitioned to the subgrid. We can clearly see that the patch leads to a Ψ_{cg} that is much smoother than what was obtained using the switching function.

Figure 3 gives another example of the partitioning where we have considered the $6a_1$ (HOMO-2) orbital of O_3 that is composed of atomic 2p orbitals in the plane of the three oxygens and is part of the representation of lone pair electrons in the terminal oxygens.⁴² This orbital has a more complicated angular dependence near each nucleus and thus requires a more typical number of subgrid partial waves.

Figure 4 is a convergence study of the normalization of the $6a_1$ orbital that illustrates how the patch algorithm enables a monotonic improvement in the accuracy of the partial wave expansion as the angular momentum cutoff $\ell_{\max}$ increases in both the central and subgrid regions. Specifically, the normalization of the $6a_1$ orbital improves with increasing $\ell_{cg,\max}$ and reaches eight figures accuracy with $\ell_{cg,\max} = 50$, when then number of terms included in the polynomial radial patch functions is $n = 3$. The normalization also improves with increasing $\ell_{sg,\max}$, with the difference between $\ell_{sg,\max}=2$ and $\ell_{sg,\max}=3$ being less than 10^{-7} . Note that with $n = 5$, it is possible obtain ten figures accuracy. In applications to solving the scattering equations discussed in Section 4, we

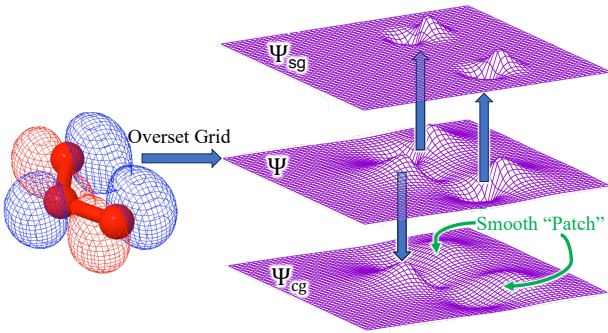


Figure 3: Decomposition of the total wave function, Ψ , into subgrid partitions, Ψ_{sg} , and the central grid partition, Ψ_{cg} , of the $6a_1$ orbital of O_3 . The patch algorithm leaves the p orbital on the middle oxygen atom, which is located at the origin, on the central grid and puts the nodal structure of the p orbitals centered on the outer oxygen atoms on the subgrids.

will choose $\ell_{sg,\max}=3$ and $n = 3$ which yields final cross section which can be converged to better than 0.5% with rather modest values of $\ell_{cg,\max}$. We have also considered the sensitivity of the expansion to the location of the central grid. In Figure 4 we give the results locating the origin of the central grid on the center-of-charge of the molecule, which is equidistant from the two terminal O atoms and 0.45 Å from the central O atom. We can see that the accuracy does not strongly depend on the location of the central grid, including centering it within a subgrid as in this example where it is located inside the subgrid for the central O atom. In this case, the convergence of the expansion with respect to the central grid $\ell_{cg,\max}$ of the $6a_1$ orbital is slightly faster than when we centered the central grid on the central O atom. This result is expected since the distance to the terminal O atoms is reduced by the shift of the central grid, leading to faster convergence with respect to $\ell_{cg,\max}$, as will be discussed in Section 4.1 below. We note that when an atom is at the origin of the central grid there is no need to have a subgrid for that atom, thus reducing computational effort.

As noted above, we use eq (10) to construct the central-grid wave function because it implicitly retains the subgrid truncation error $\epsilon(\mathbf{r})$. If instead we calculate only the first sum in eq (11), which is labeled “patch”, and thereby place only the patch itself on the central grid, we obtain the red dashed curve in Figure 4. In this case, the normalization error plateaus at $\sim 10^{-4}$ for $\ell_{cg,\max} = 15$. In contrast, implicitly including $\epsilon(\mathbf{r})$ by using eq (10) allows for accurate results to be obtained with only a small partial-wave expansion of the subgrid function.

3 Complex Kohn Method

Since its introduction,⁴³ the Kohn variational method has been applied to a range of quantum scattering problems, from nuclear collisions to electron scattering and photoionization of atoms and molecules. The complex Kohn method, which was developed later, uses complex-valued S -matrix or T -matrix bound-

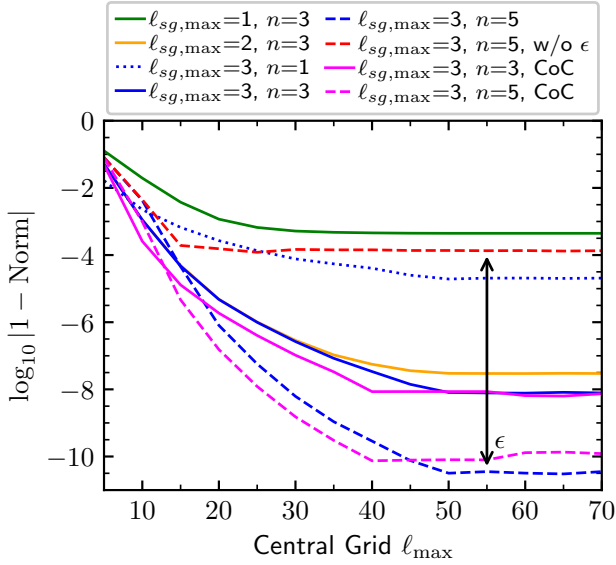


Figure 4: Convergence test of the normalization error for the projection of the $6a_1$ orbital of O_3 onto spherical harmonics with $\ell_{cg,max}$, where $\ell_{cg,max}$ is the maximum angular momentum quantum number on the central grid. We show the results for $\ell_{sg,max} = 1, 2, 3$ on the subgrids and a different number of terms included in the polynomial patch, $n = 1, 3, 5$ as defined in eq (7). The central grid with radius of $6.0 \text{ \AA}$ is centered on the central oxygen atom with one subgrid with radius of $0.6 \text{ \AA}$ placed on each of the remaining oxygens. The red dashed line (labeled "w/o ϵ ") does not include the subgrid truncation error ϵ , see the text. There are also two curves, labeled "CoC", where the center of the central grid was moved to the center of charge, which is located at $0.45 \text{ \AA}$ from the central O atom. All three subgrids have the same radius of $0.6 \text{ \AA}$.

ary conditions^{3,5,6,21–24,44,45} to eliminate spurious numerical singularities at discrete energy eigenvalues found in early implementations of the Kohn principle in atomic and molecular scattering. In Section 3.1, we briefly review the central ideas of the complex Kohn variational approach. Section 3.2 discusses how the scattering boundary conditions within the variational approach are imposed using overset grids.

3.1 Complex Kohn Variational Principle

In the case of scattering with only a single electronic target state, which is the basic situation considered in our numerical tests, the T matrix (proportional to the scattering amplitude) for electron scattering from incident momentum $\mathbf{k}$ to final momentum $\mathbf{k}'$ is:

$$T_{\mathbf{k}',\mathbf{k}}^+ = \langle \psi_{\mathbf{k}'}^0 | \hat{V} | \psi_{\mathbf{k}}^{(+)} \rangle, \quad (12)$$

where $\psi_{\mathbf{k}}^{(+)}$ is the exact scattering wave function and $\psi_{\mathbf{k}'}^0$ is the unperturbed initial state, labeled by asymptotic momenta $\mathbf{k}$ and $\mathbf{k}'$. The wave functions in this expression are functions of the coordinates of all the electrons in the system, as are the wave functions in the general multichannel case. The building block of the general problem is the single-channel case using the static-exchange approximation which treats the target as a single configuration of occupied molecular orbitals and reduces the problem to that of a single electron in the field of the non-local potential, $\hat{V}$. For example, for photoionization from a closed shell molecule we have

$$\hat{V} = V_{\text{nuc}} + \sum_d (2\hat{J}_d - \hat{K}_d) + \hat{J}_s + \hat{K}_s. \quad (13)$$

Here, V_{nuc} is nuclear attraction, $\hat{J}$ and $\hat{K}$ are the direct and (nonlocal) exchange operators, s and d refer to singly occupied and doubly occupied orbitals, respectively.

The complex Kohn variational principle treats this problem (and the general one) by optimizing a trial scattering wave function, $\psi_k^{(\pm)t}$, which satisfies the scattering boundary conditions, to find the stationary point of the variational expression,

$$T_{\mathbf{k}',\mathbf{k}}^{+S} = T_{\mathbf{k}',\mathbf{k}}^+ + (2\pi)^{-3/2} \langle \psi_{\mathbf{k}'}^{(-)t} | \hat{H} - E | \psi_{\mathbf{k}}^{(+t)} \rangle. \quad (14)$$

In eq (14) the trial functions $\psi_{\mathbf{k}'}^{(-)t}$ and $\psi_{\mathbf{k}}^{(+t)}$ represent the continuum wave function under outgoing (+) and incoming (−) spherical-wave boundary conditions and are labeled by asymptotic momenta.

In electron scattering or photoionization of

a polyatomic molecule, the scattering wave function requires relatively few partial waves asymptotically, and their number determines the size of the T matrix in the angular momentum representation. So we write the scattering wave functions, related by $\psi_{\mathbf{k}}^{(-)} = (\psi_{-\mathbf{k}}^{(+)})^*$, as an expansion in asymptotic partial waves labeled by angular momentum quantum numbers l and m as

$$\psi_{\mathbf{k}}^{(\pm)}(\mathbf{r}) = \sqrt{\frac{2}{\pi}} \sum_{l,m}^{l_{a,\max}} i^l \psi_{klm}^{(\pm)}(\mathbf{r}) Y_{lm}^*(\hat{\mathbf{k}}), \quad (15)$$

where the Y_{lm} 's are spherical harmonics, the asymptotic electron kinetic energy is $E = k^2/2$, and the sum is truncated at a maximum $\ell_{a,\max}$ which depends on the scattering energy and the size of the molecule. Then the T matrix in the momentum representation is related to these wave functions by

$$T_{\mathbf{k}',\mathbf{k}}^+ = \sum_{l',m',l,m} (i)^{(l-l')} \frac{2}{\pi} T_{k,l',m',l,m}^+ Y_{l',m'}(\hat{\mathbf{k}}) Y_{l,m}^*(\hat{\mathbf{k}}),$$

$$T_{k,l',m',l,m}^+ = \langle \psi_{kl'm'}^0 | \hat{V} | \psi_{klm}^+ \rangle. \quad (16)$$

In terms of these functions, the complex Kohn variational expression for $T_{k,l',m',l,m}^+$, the T matrix labeled by initial and final angular momenta of the scattered electron, is then

$$T_{k,l',m',l,m}^{+S} = T_{k,l',m',l,m}^{+t} + \langle \psi_{kl'm'}^{(-)t} | \hat{H} - E | \psi_{klm}^{(+t)} \rangle. \quad (17)$$

With eq (17) we are ready to write the working equations of the complex Kohn approach, and finally see how they are implemented in the overset-grid representation.

Previous implementations of the complex Kohn method^{3-6,19-24} use a specific form of the trial function that represents the scattering function in the vicinity of the molecule by an expansion in square-integrable orbitals, in turn expanded in Gaussian basis functions. Further, terms asymptotically proportional to Riccati-Bessel functions are added to the square-integrable functions. The variational expression in eq (17) involves a trial scattering amplitude, $T_{k,l',m',l,m}^{+t}$ that also appears in the trial wave

function:

$$\begin{aligned} \psi_{klm}^{(\pm)t}(\mathbf{r}) = & \sum_i c_i^{(\pm)} \psi_i(\mathbf{r}) \\ & + \frac{1}{kr} \left[\hat{j}_l(kr) Y_{lm}(\hat{\mathbf{r}}) \right. \\ & \left. + \sum_{l',m'} T_{k,l',m',l,m}^{\pm t} \tilde{h}_{l'}^{\pm}(kr) Y_{l'm'}(\hat{\mathbf{r}}) \right], \end{aligned} \quad (18)$$

where $\hat{j}_l(kr)$ is a regular Riccati-Bessel function and $\tilde{h}_{l'}^{\pm}(kr) \xrightarrow{r \rightarrow \infty} \hat{h}_{l'}^{\pm}(kr)$ is a function regular at the origin that goes asymptotically to a Riccati-Hankel function. In eq (18), the set of coefficients, $\{c_i\}$, and the trial values of the T -matrix elements, $T_{k,l',m',l,m}^{\pm t}$, are the variational parameters.

The essence of the complex Kohn method is to set the derivatives of eq (17) with respect to the variational parameters in the trial function to zero, and thereby produce the variationally stationary approximation for the T matrix,

$$\mathbf{T}^S = \mathbf{N}_{00} - \mathbf{N}_{0q} \mathbf{M}_{qq}^{-1} \mathbf{N}_{q0}. \quad (19)$$

In eq (19) the subscript 0 denotes the set of regular functions, $\{\hat{j}_l(kr) Y_{lm}(\hat{\mathbf{r}})/kr\}$ and q denote the expansion basis of Gaussian orbitals and Hankel functions, $\{\{\psi_i(\mathbf{r})\}, \{\tilde{h}_l^{\pm}(kr) Y_{lm}(\hat{\mathbf{r}})/kr\}\}$. The first term on the right is the Born term,

$$(\mathbf{N}_{00})_{l',m',l,m} = \left\langle \frac{\hat{j}_{l'}(kr)}{kr} Y_{l'm'}(\hat{\mathbf{r}}) \left| \hat{V} \right| \frac{\hat{j}_l(kr)}{kr} Y_{lm}(\hat{\mathbf{r}}) \right\rangle \quad (20)$$

and the matrices $\mathbf{N}_{0q}$ and $\mathbf{N}_{q0}$ are defined similarly with $\tilde{h}_l^{(+)}(kr)$ functions in the q basis on the right and $\tilde{h}_l^{(-)}(kr)$ functions in the q basis on the left. The matrix $\mathbf{M}_{qq}$ is the matrix of $(H - E)$ in the expansion basis, again with $\tilde{h}_l^{(+)}(kr)$ functions in the q basis on the right and $\tilde{h}_l^{(-)}(kr)$ functions in the q basis on the left. These are the traditional complex Kohn working equations, which have the same form in the general multichannel case of inelastic scattering, and which are described in the references,^{3-6,19-24} where the technical questions of the evaluation of the matrix elements

in this mixed basis of Gaussian functions and Bessel functions are addressed. We emphasize here that there are no singularities in the inverse matrix $\mathbf{M}_{qq}^{-1}$ at real energies. This property is ensured by the complex-valued scattering boundary conditions for outgoing and incoming waves, enforced in the trial function.

3.2 Overset-Grid Implementation of the complex Kohn Equations

The expansion basis, denoted by the index q in the complex Kohn working expression for the T matrix in eq (19) is the key to imposing the outgoing and incoming wave boundary conditions in the trial function. In our overset-grid representation of a general wave function $\Psi(\mathbf{r})$, we must do the same. In the overset-grid method, we define a trial wave function with the incoming boundary condition directly included in the partial wave expansion via the function $\phi_{klm}^0(\mathbf{r})$, and add to that term a group of functions that *all* behave asymptotically as pure outgoing (or incoming) proportional to combinations of Hankel functions $\hat{h}_l^{(\pm)} Y_{lm}(\hat{\mathbf{r}})/kr$. The overset-grid trial function, replacing eq (18), is

$$\psi_{klm}^{(\pm)t}(\mathbf{r}) = \phi_{klm}^0(\mathbf{r}) + \sum_{i=1}^N c_i \phi_{i,klm}^{(\pm)}(\mathbf{r}), \quad (21)$$

where,

$$\phi_{klm}^0(\mathbf{r}) = \hat{j}_l(kr) Y_{lm}(\hat{\mathbf{r}})/kr \quad (22)$$

and the scattered-wave basis is

$$\phi_{i,klm}^{(\pm)}(\mathbf{r}) \equiv \left(\hat{G}_0^\pm \hat{V} \right)^i \phi_{klm}^0(\mathbf{r}), \quad (23)$$

in which $\hat{j}_l(kr)$ denotes the regular Riccati-Bessel function as the incoming wave, and G_0 is the one-body free-particle scattering Green's function. The essential idea is the expansion in eq (21) of the scattered wave in terms of the numerically generated functions, $\phi_{i,klm}^{(\pm)}(\mathbf{r})$. The $\phi_{i,klm}^{(\pm)}(\mathbf{r})$ are obtained by repeated applications of the operator product $\hat{G}_0^\pm \hat{V}$ on the incoming wave, $\phi_{klm}^0(\mathbf{r})$. These functions would gener-

ate a Born series of order N for the scattering wave function in eq (21). Finally, these functions are orthogonalized to form the iterates of the Arnoldi algorithm^{1,2} which are then the q basis set used to evaluate eq (19).

This expansion relies on the asymptotic properties of the free-particle Green's function, familiarly defined by the relations (atomic units)

$$\begin{aligned} G_0^\pm(\mathbf{r}, \mathbf{r}') &\equiv -\frac{1}{2\pi} \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \\ &= \frac{1}{r r'} \sum_{lm} Y_{lm}(\theta, \phi) Y_{lm}(\theta', \phi') g_{0,l}^\pm(r, r'), \\ g_{0,l}^\pm(r, r') &= -\frac{2\mu}{k} \hat{j}_l(kr_{<}) \hat{h}_l^\pm(kr_{>}). \end{aligned} \quad (24)$$

The last line of eq (24) displays why, after operating on any function, $G_0^\pm$ produces a complex-valued function that is a linear combination of purely outgoing or incoming spherical waves of various angular momenta.

Using the expansion in eq (21) in the complex Kohn variational principle, and setting the derivatives with respect to the coefficients c_i to zero, produces a working equation for the T matrix with exactly the same form as eq (19). The only difference is that the subscripts q on the matrices refer to the set of numerically determined functions $\{\phi_{i,klm}^{(\pm)}(\mathbf{r})\}$.

To finish the implementation of the overset-grid method, we need algorithms to operate with $G_0^\pm$ and the non-local static-exchange potential, $\hat{V}$, on a function represented on the grid as previously described in Section 2 to produce a new overset-grid representation of the result. Those algorithms are described in detail and demonstrated in Greenman et al.¹ and Marante et al.,² so we omit them in this brief overview, except to say that they make explicit use of the FEM-DVR basis of radial functions in each subgrid and the quadratures associated with it.

Nevertheless, we make two important technical observations about the overset-grid implementation here:

1. The free-particle Green's function is translationally invariant, because it is a function only of $\mathbf{r} - \mathbf{r}'$ as eq (24) shows.

Thus the same algorithm for the application of $G_0^\pm$ works on the central grid *and* all the subgrids. With respect to any center, the free-particle Green’s function’s operation has the same form.

2. The result of using N terms (Born-Arnoldi basis functions) in the trial function produces a result from the expression for the T matrix in eq (19) that is an $[(N - 1)/N]$ Padé approximant in orders of the potential, $\hat{V}$, to the scattering T matrix. Consequently the T matrix expression produces a result that generally converges rapidly with adding terms in that expansion.

Finally, the choices of the subgrids and finite elements are described in Section 4 for each of our computational examples. Those choices are in the context of an optimization of the angular basis described in the two earlier papers^{1,2} on the overset-grid method, whereby different maximum ℓ values, less than a maximum $\ell_{cg,max}$, can be used in the spherical shells of the central grid formed by the radial finite elements.

Applying this method to the calculation of the photoionization cross section, as we have done in the following sections, requires another step. The fully differential photoionization cross section to produce ion state Γ_0 is proportional to the square modulus of the dipole matrix element between the neutral and electron-ion scattering wave functions:

$$\frac{d^2\sigma^{\Gamma_0}}{d\Omega_{\mathbf{k}_{\Gamma_0}} d\Omega_{\hat{\mathbf{n}}}} = \frac{8\pi\omega}{3c} \left| \langle \Psi_0 | \hat{\mathbf{n}} \cdot \boldsymbol{\mu} | \Psi_{\Gamma_0, \mathbf{k}_{\Gamma_0}}^{(-)} \rangle \right|^2, \quad (25)$$

which defines the differential cross section for linear polarization $\hat{\mathbf{n}}$, ejected electron momentum $\mathbf{k}_{\Gamma_0}$, and photon energy ω . The complex Kohn scattering calculation produces the final state wave function $\Psi_{\Gamma_0, \mathbf{k}_{\Gamma_0}}^{(-)S}$ in this expression (for a single channel in our examples), but that wave function satisfies incoming Coulomb scattering boundary conditions. The Coulomb Green’s function is *not* translationally invariant, and so our overset-grid algorithm for the operation of $G_0^\pm$ on the grid does not apply to that case. A matching algorithm to transform

from short range (non-Coulomb) to Coulomb scattering boundary conditions corrects that problem and is described in detail by Marante et al.² That algorithm was used in photoionization calculations described in the following sections. A final point about complex Kohn calculations of the photoionization amplitude is that when the matrix element in eq (25) is evaluated with the Kohn trial function using its variationally determined parameters, it is itself a variational approximation to the photoionization amplitude, as pointed out by Orel and Rescigno.⁴⁶

4 Results

We implemented the patch algorithm for the complex Kohn variational method based on the overset-grid version of **ePolyScat** that was created during the development of the switching function algorithm reported by Greenman et al.¹ and Marante et al.² This code suite provides interfaces to several distributed quantum chemistry codes, including **MOLPRO**^{47–49} and **GAUSSIAN**⁵⁰ for Hartree-Fock and post-Hartree-Fock methods.

In this section, we offer four different tests of the patch algorithm. To make a systematic comparison of the convergence of the patch and switching function algorithms, we begin with a relatively simple case, electron scattering from the neon dimer. In this case, we can vary the geometry over a larger range of internuclear distances without changing the character of the target electron state than would be possible in a covalently bonded molecule. We then see how the patch-algorithm modification of overset grids treats subgrids with increasing distant from the origin of the central grid. We then discuss two cases used previously as tests of the original switching function algorithm, electron- CF_4 scattering studied by Greenman et al.¹ and photoionization from the $\text{F}(1s)$ orbital of CF_4 from the Marante et al.² study of the applicability of the static-exchange approximation in cases with symmetrically equivalent atoms. Finally, we turn to a larger molecular example, photoionization of the $\text{N}(1s)$ orbital of pyridine

(C₅H₅N) that is a target of recent experiments.

4.1 Electron Scattering from the Neon Dimer

Physically larger molecular targets in electron scattering require larger numbers of partial waves simply because they scatter electrons with larger impact parameters, b , whose angular momenta would be given by the classical expression $\ell = pb$ where p is the electron’s momentum. These considerations control the $\ell_{a,\max}$ needed in the partial wave expansion given in eq (15) as is common to any scattering method that uses an asymptotic partial-wave expansion of the wave function. Thus, when computing the scattering from the neon dimer, Ne₂, the limits of the expansion of the central grid, $\ell_{cg,\max}$, must be at least as large as $\ell_{a,\max}$ in the asymptotic region. The calculation on Ne₂ allows us to investigate the value of $\ell_{cg,\max} > \ell_{a,\max}$ needed to represent parts of the wave function left on the central grid in the vicinity of the subgrids as a function of the internuclear distance d .

For this test, the target state of the neon dimer was prepared at three internuclear distances: $d = 3.0$ Å, 4.5 Å, and 6.0 Å, ranging from near the equilibrium distance (3.1 Å^{51,52}) to about twice the equilibrium bond length. The target orbitals were Hartree-Fock orbitals computed with the MOLPRO package using a correlation-consistent polarized valence triple-zeta basis set⁵³ (cc-pVTZ). For comparison between the patch and switching function algorithms, the central grid was placed at the midpoint between the two neon atoms, with subgrids built around each atom. We tested two subgrid radii: $r_{sg,\max} = 1.0$ Å and $r_{sg,\max} = 0.5$ Å, which represent scenarios where the subgrids are sufficient to cover the majority of the atomic electron density or restricted to a region containing only the nuclear cusps and inner portions of the occupied orbitals, respectively.

The subgrids with $\ell_{sg,\max} = 3$ were adaptively divided into 12 finite elements for $r_{sg,\max} = 1.0$ Å or 11 finite elements for $r_{sg,\max} = 0.5$ Å, with the size of the smallest finite element near the neon atom being around 0.0029 Å. The cen-

tral grid with a radius of 8.3 Å was split into 56 finite elements with a width of 0.00142 Å for the smallest element near the origin. Each finite element of every grid contained 8th order Gauss-Lobatto DVR functions. Small radial elements are necessary to accurately represent the cusps of atomic orbitals and the results of the action of the potential in eq (13) and the free particle Green’s function on similar cusps in the continuum wave function. As explained in the previous overset-grid studies,^{1,2} the maximum angular momentum in each finite element shell of the central grid was adaptively varied and increased to $\ell_{cg,\max}$ near the subgrids. The maximum asymptotic angular momentum quantum number included in the scattering T matrix was $\ell_{a,\max} = 10$, regardless of the maximum angular momentum on the central grid.

Figure 5 shows the convergence behavior of the two methods with respect to $\ell_{cg,\max}$ on the central grid, while the subgrid angular momentum was fixed at $\ell_{sg,\max} = 3$ and $n = 3$ for all cases, based on the good convergence properties seen in Figure 4 with these parameters. In panel (a) of Figure 5, we also show the results from a purely single-center expansion calculation (including only the central grid with high $\ell_{\max}$ and using the Schwinger variational approach^{7,8}) that requires $\ell_{\max} \geq 200$ to approach convergence to the correct result even at the smallest internuclear distance. In the limit of very large separation between the two Ne atoms, the scattering should approach twice the cross section of a single Ne atom, which is plotted as the solid green line in panels (c) and (f). We can see that above 10 eV the scattering with $d = 6.0$ Å is indeed very close to twice the atomic cross section. At lower energies and at smaller values of d , the scattering from the dimer has structure from multiple scattering that is not in the atomic scattering cross section.

In Table 1 we give the value of $\ell_{cg,\max}$ where two successive lines appear to be on top of each other. In Table 2 we give the corresponding numerical cross section convergence data at 5.0 eV and 20.0 eV. Comparing the results in these two tables indicates that the visual comparison provided by Figure 5 corresponds to a residual

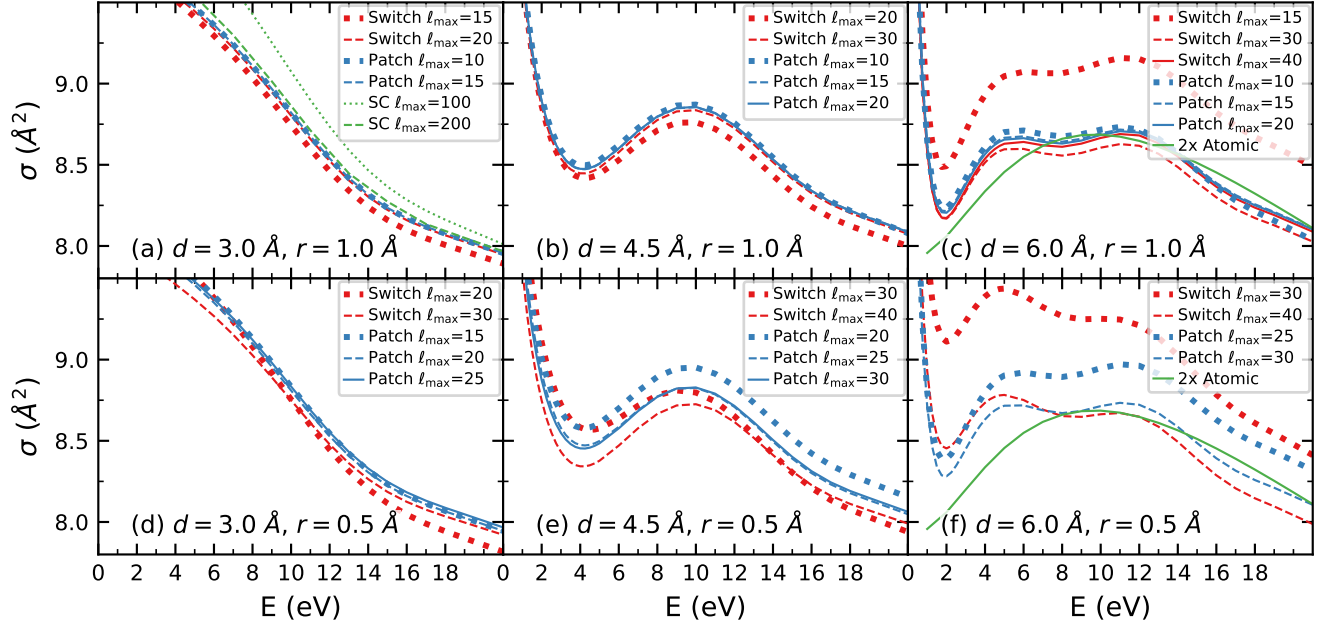


Figure 5: Total electron scattering cross section, σ , of the neon dimer as a function of the asymptotic electron kinetic energy, E , comparing calculations with the patch (with $n = 3$ as defined in eq (7)) and switching function algorithms. In both patch and switching functions calculations, $\ell_{sg,max} = 3$. The internuclear distance, d , increases from left to right. The upper row (panels a, b, c) presents calculations with a subgrid radius of $r = 1.0$ Å; the lower row (panels d, e, f) corresponds to $r = 0.5$ Å. The total cross section for electron scattering from atomic neon (scaled by a factor of two) is shown as the solid green line in panels (c) and (f). Single-center calculations in panel (a) are labeled by SC.

Table 1: Value of $\ell_{cg,max}$ when the cross sections given in Figure 5 have converged to within 0.5% as a function of $r_{sg,max}$ and $r_{sg,0} = d/2$. The values in parentheses are estimated using eq (26) with $C_{Patch} = 6.7$ and $C_{Switch} = 13.3$

Grid	$r_{sg,0}$	$r_{sg,max}$	$\ell_{cg,max}$
Patch	1.5	1.0	10
	2.25	1.0	15
	3.0	1.0	20
	1.5	0.5	20
	2.25	0.5	30
	3.0	0.5	(40)
Switch	1.5	1.0	20
	2.25	1.0	30
	3.0	1.0	40
	1.5	0.5	(40)
	2.25	0.5	(60)
	3.0	0.5	(80)

error of $< 0.5\%$. In Fig. 6 we indicate the angle α which a subgrid subtends with respect to the center of the central grid and is proportional to $\frac{r_{sg,max}}{r_{sg,0}}$. Now the value of ℓ of the spherical harmonics needed resolve the subgrid patch is related to α by $\ell_{cg,max} \propto \frac{1}{\alpha}$. Then relationship between $r_{sg,0}$, $r_{sg,max}$, and $\ell_{cg,max}$ can be expressed as

$$\ell_{cg,max} \approx C_{Grid} \frac{r_{sg,0}}{r_{sg,max}}, \quad (26)$$

where using the 0.5% criterion we have $C_{Patch} = 6.7$ and $C_{Switch} = 13.3$. The parenthetical values given in Table 1 could not be determined from Figure 5 but instead were computed using eq (26) and the values of C_{Grid} indicated above. It is expected that for either the switch or patch methods, smaller residual errors would be obtained with larger values of C_{Grid} .

To summarize the results of this e -Ne₂ scattering section, we find that the value of $\ell_{cg,max}$

Table 2: Convergence of total electron scattering cross sections with respect to $\ell_{cg,\max}$ for the static-exchange potential of Ne₂ at $d = 6.0$ Å using the patch with $n = 3$ and switching function algorithms, both with $\ell_{sg,\max} = 3$. Results are shown for two subgrid radii ($r_{sg,\max} = 1.0$ Å and $r_{sg,\max} = 0.5$ Å) at electron energies of 5.0 eV and 20.0 eV. Cross sections are reported in Å², with relative errors, shown as a percentages, compared to the $\ell_{cg,\max} = 70$ results using the patch algorithm at the same scattering energy E . The boxed data indicate the errors when the $\ell_{cg,\max}$ given in Table 1 for $r_{sg,0} = d/2 = 3.0$ Å was used.

E	$\ell_{cg,\max}$	$r_{sg,\max} = 1.0$ Å				$r_{sg,\max} = 0.5$ Å			
		Switching Function		Patch		Switching Function		Patch	
20 eV	10	9.382	17.7%	7.929	-0.5%	17.514	119.7%	14.190	78.0%
	20	7.982	0.1%	7.974	0.0%	10.578	32.7%	8.787	10.2%
	30	7.900	-0.9%	7.972	0.0%	8.290	4.0%	7.979	0.1%
	40	7.960	-0.2%	7.972	0.0%	7.867	-1.3%	7.970	0.0%
	50	7.974	0.0%	7.972	0.0%	7.882	-1.1%	7.997	0.3%
	60	7.974	0.0%	7.972	0.0%	7.957	-0.2%	7.997	0.3%
	70	7.973	0.0%	7.972	0.0%	7.999	0.3%	7.995	0.3%
5 eV	10	10.463	20.9%	8.701	0.5%	44.833	417.9%	21.944	153.5%
	20	8.667	0.1%	8.655	0.0%	11.737	35.6%	9.449	9.2%
	30	8.596	-0.7%	8.657	0.0%	9.437	9.0%	8.716	0.7%
	40	8.630	-0.3%	8.657	0.0%	8.783	1.5%	8.662	0.1%
	50	8.654	0.0%	8.657	0.0%	8.575	-0.9%	8.681	0.3%
	60	8.659	0.0%	8.657	0.0%	8.584	-0.8%	8.690	0.4%
	70	8.659	0.0%	8.657	0.0%	8.648	-0.1%	8.688	0.4%

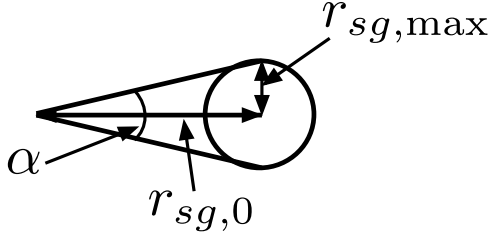


Figure 6: Sketch of the angle, α , subtended by a subgrid with radius $r_{sg,max}$ as seen from the origin of the central grid at a distance $r_{sg,0}$.

needed to obtain a certain level of convergence can be predicted using eq (26). The estimate of $\ell_{cg,max}$ using eq (26) is valid for both the switching algorithm and the patch algorithm. We see that the values of C_{Grid} , which we have found here, imply that the patch algorithm requires half as large a value of $\ell_{cg,max}$ compared to that needed for the switch algorithm for the same accuracy. Given that the total number of partial waves scales as $\ell_{cg,max}^2$, the patch algorithm requires one fourth the number of partial waves compared to the switch algorithm. In subsequent sections we will explore the wider applicability of eq (26) by considering both electron scattering and photoionization in a few molecular systems.

4.2 Electron Scattering from CF_4

Our second test case, electron scattering from CF_4 , is the one chosen in the first published demonstration of the overset-grid algorithm by Greenman et al.¹ The target electronic ground state of CF_4 was calculated at the Hartree-Fock level with a 6-31G* basis set^{54–56} with a C–F bond length of 1.315 Å (used in the previous study) and produced a total electronic energy of -435.48378 hartrees for the closed-shell 1A_1 state.

For scattering calculations, the full molecular symmetry T_d was reduced to the Abelian subgroup D_2 , and the scattering wave functions were symmetrized accordingly. We chose the same grids as Greenman et al.,¹ that is, the central grid centered on the carbon atom with a radius of 5.31 Å were divided into 27 finite elements with the smallest element be-

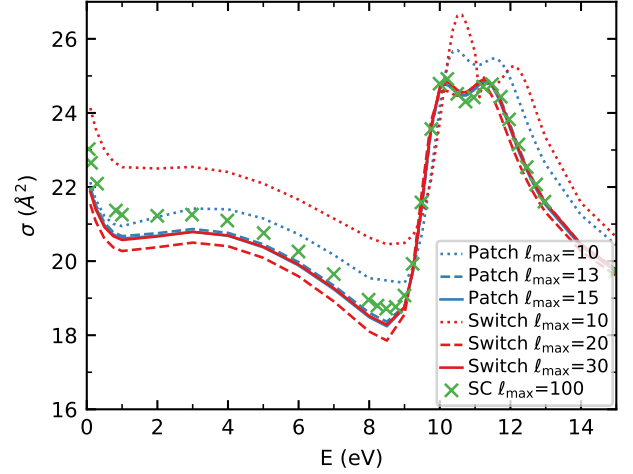


Figure 7: Comparison of the total scattering cross sections for the static-exchange potential of CF_4 . The results for the overset-grid patch algorithm (blue dotted, dashed, and solid lines) are shown for subgrids with $\ell_{sg,max} = 3$, $n = 3$, and central grid with $\ell_{cg,max} = 10, 13$, and 15. All cross-section features converge at $\ell_{cg,max} = 15$, while the switching function method with the same subgrid $\ell_{sg,max}$ converges at $\ell_{cg,max} = 30$ on the central grid. The Schwinger method with single-center expansion (SC) is not yet completely converged at $\ell_{max} = 100$. The maximum angular momentum quantum number included in the scattering T matrix is $\ell_{a,max} = 6$.

ing 0.00336 Å near the origin. Identical subgrids with $\ell_{sg,max} = 3$, $n = 3$, and a radius of 0.60 Å were used around each fluorine atom with 14 finite elements and the smallest element of 0.00236 Å. Each finite element of the central grid and subgrids was expanded by the Gauss-Lobatto basis functions of 12th order. With these values of $r_{sg,0} = 1.315$ Å and $r_{sg,max} = 0.6$ Å, eq (26) predicts good convergence with $\ell_{cg,max}^{Patch} = 15$ and $\ell_{cg,max}^{Switch} = 30$.

Figure 7 shows the total cross section calculated in the static-exchange approximation using both algorithms. The double peak between 10 and 12 eV is due to a pair of shape resonances^{1,7,57}, a 2T_2 resonance (in the full T_d symmetry) at about 10.0 eV and a 2A_1 resonance at about 11.5 eV. The result of a single-center calculation is also shown in Figure 7 with $\ell_{max} = 100$. The single-center expansion, which involves of the order of ℓ_{max}^2 partial waves, gen-

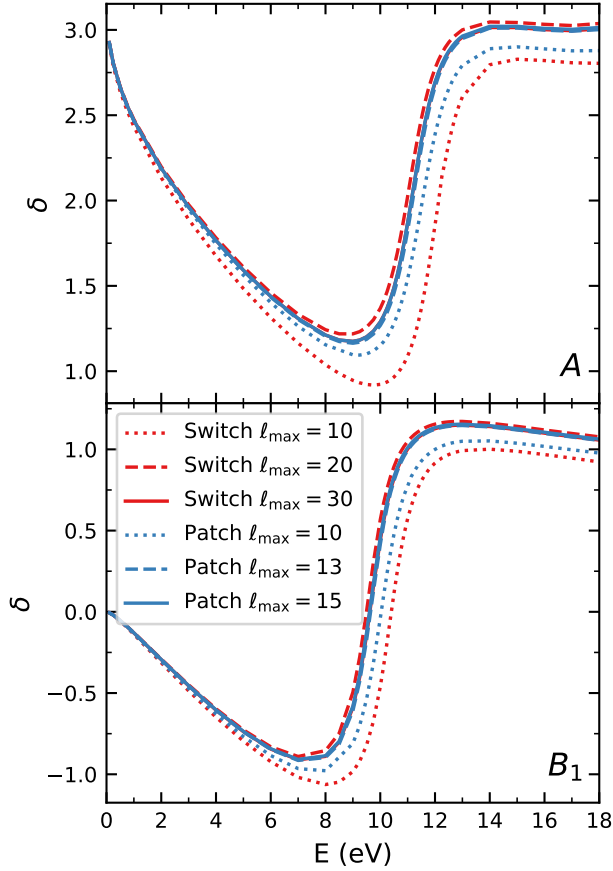


Figure 8: Convergence of the eigenphase sums computed with the patch and switch algorithms near the two resonances in electron scattering from CF_4 using the same subgrid parameters as in Figure 7. Note that the calculations were performed using the abelian subgroup D_2 of the full T_d symmetry. The upper panel gives the results for the A scattering symmetry which corresponds to the sum of the A_1 , A_2 , and E symmetries in the T_d point group. The lower panel gives the B_1 symmetry results which corresponds to the sum of one of the three equivalent T_2 and T_1 contributions in T_d . The rapid rises identify and mark the locations of the 2A_1 (higher energy) and 2T_2 (lower energy) resonances in Figure 7.

erally converges slowly after reproducing the qualitative shape of the total cross section. Consequently, here and in our other comparisons, the single-center results converge to only a few percent. In Figure 7 the patch algorithm accurately reproduces the double peak and the minimum preceding it with only $\ell_{\text{max}} = 15$ on

the central grid where the entire cross section up to 13 eV also converges, demonstrating a reduction of $\ell_{\text{cg,max}}$ by half from the switching function approach, as predicted by eq (26), and by at least an order of magnitude from the single-center expansion approach for a converged variational answer.

The convergence of the two overset-grid algorithms near the resonances is seen more clearly in the behavior of the eigenphases of the scattering S matrix in the symmetries of the resonances. In scattering theory for electron collisions from atoms, the asymptotic form of the wave function can be characterized by a scattering phase shift, δ . In a narrow resonance, due to the presence of a metastable state, the phase shift will rise rapidly through π as a function of energy. In molecules where many different partial waves couple to a resonance, the equivalent quantity is the eigenphase sum δ_{sum} , which is obtained by diagonalizing the S matrix and summing the phases, divided by two, of the resulting eigenvalues.⁵⁸ The calculations presented here were performed in D_2 symmetry. In that symmetry, there are two shape resonances at different energies with one with A symmetry and one with B_1 symmetry, corresponding to the two peaks in the cross section seen in Figure 7.

In Figure 8 we plot the eigenphase sums in the A and B_1 symmetry. Rapid rises in the eigenphase sums (which would be a rise of π for a narrow resonance) mark the positions of these two resonances. In particular, the energy of the center of these rises give the energies of the resonances, and the range of energies over which the rises occur give the widths of the resonances, which are inversely proportional to the lifetimes of the resonances. The fact that these two eigenphase sums rise by less than π is the result of the rapidly dropping non-resonant background Coulomb scattering phase shifts. Again, the positions and widths of the resonances computed with the patch algorithm are seen to converge with half the number of partial waves necessary for the switching-function algorithm. The computational effort scales as $\approx \ell^3$, so that a reduction of a factor of two in the number of partial waves could lead to a reduc-

tion by a factor of eight in the computational effort.

4.3 F(1s) Photoionization of CF₄

As the first test of the patch algorithm in photoionization calculations, we return to the F(1s) ionization of the CF₄ molecule studied by Marante et al.² with the switching-function algorithm. For consistency, we used the same triple zeta Gaussian with polarization basis set^{59,60} with three additional *s*-type Gaussians, with exponents 0.08, 0.04, and 0.02, and two *p*-type Gaussians, with exponents 0.05 and 0.01, at the center of the molecule. In this case, the radius of the central grid was extended to² 19 Å, containing more finite elements accordingly. Other grid parameters are the same as for the electron scattering case in Section 4.2, which are consistent with the earlier study.²

The fluorine atoms are equivalent, and the 1s orbitals form an *a*₁ and a degenerate set of *t*₂ orbitals in *T_d* symmetry. This example was part of a study of the localization of the core hole in the fluorine ionization of CF₄ (which is accomplished by a very slight extension of one bond² in the Hartree-Fock calculation on the neutral molecule) and reduces the symmetry to C_{3v}. A principal conclusion of Marante et al.² was that uncoupled localized-hole calculations can accurately replace a coupled channel scattering calculation using degenerate delocalized core orbitals.

Convergence studies of both the total photoionization cross section and the energy-dependent asymmetry parameter β are shown in Figure 9. The asymmetry parameter appears in the standard formula⁶¹ for the differential photoabsorption cross section averaged over molecular orientations at a fixed energy,

$$\frac{d\sigma}{d\Omega_{\mathbf{k}}} = \frac{\sigma}{4\pi} [1 + \beta P_2(\cos \theta)] \quad (27)$$

where σ is the total cross section, P_2 is a Legendre polynomial of order 2, and θ is the angle between the polarization of light and the direction of emission of the photoelectron, $\mathbf{k}$.

The converged result in Figure 9 for the to-

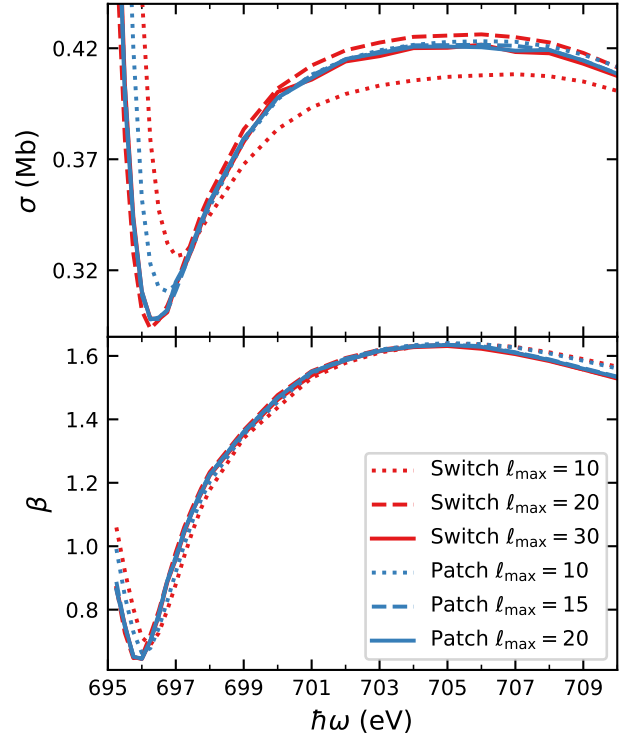


Figure 9: Convergence of the length gauge total cross sections σ_L and asymmetry parameters β_L for fluorine *K*-edge photoionization of CF₄ using the patch and switching-function algorithms within the static-exchange approximation. Note that a factor of 4 should be applied to compare with Marante et al.² who report the total fluorine core-hole ionization cross section.

tal photoionization cross section for the localized F(1s) channel of CF₄ is obtained using the patch algorithm with $\ell_{cg,max} = 15$ on the central grid, while the switching-function approach converges at $\ell_{cg,max} = 30$, these values of converged $\ell_{cg,max}$ are again consistent the results of eq (26). The calculated cross sections show an initial increase immediately above the F(1s) ionization threshold (695.4 eV) and are followed by a Cooper minimum at around 696 eV. The details of the Cooper minimum, position and minimum, are sensitive to the parameters of the calculation. Here we see the position of the minimum is shifted by approximately 0.5 eV and 1 eV in the unconverged patch and switching function algorithm calculations, respectively, at $\ell_{cg,max} = 10$. Beyond the minimum, the cross section has a broad maximum of 705 to 710 eV that converges more rapidly. The asymme-

try parameter, also sensitive to the accuracy of the scattering solution near the Cooper minimum, quickly rises from the minimum of 0.6 at around 1 eV above the threshold to 1.6, which is close to the physical limit of 2.

4.4 N(1s) Photoionization of Pyridine

Our final test is a more demanding case of core ionization of a molecule with eleven atoms, which requires eleven subgrids around atoms of three different types. The target electronic structure of pyridine (C_5H_5N) was calculated using the Hartree-Fock level with a cc-pVTZ basis. The geometry was optimized at this level, producing a Hartree-Fock energy of -246.7794 hartree and C_{2v} symmetry. The static-exchange potential in eq (13) has the N(1s) orbital singly occupied with singlet coupling.

The central grid with a maximum radius of $8.75 \text{ \AA}$ was adaptively divided into 40 finite elements, each with an 8th order Gauss-Lobatto quadrature defining the DVR functions. The subgrids around each nucleus had radii of approximately $0.53 - 0.65 \text{ \AA}$, depending on the atom type, determined as half of the shortest internuclear distance to their neighboring atoms. The subgrids consisted of 10 or 12 finite elements roughly adapted to the local electron density with the smallest element of $0.00521 \text{ \AA}$ near the nitrogen nucleus. The subgrids all have $\ell_{sg,max} = 3$, and the patch functions are built with $n = 3$.

The maximum angular momentum included in the T matrix was $\ell_{a,max} = 8$. We have not described the convergence of Born-Arnoldi iterations to solve the complex Kohn variational equations in other examples in this study, because that question was addressed in earlier publications^{1,2} and does not differ for the patch and switching function algorithms. In general, fewer than 30 iterations are required, but we note that in this case the most slowly convergent T -matrix element (in A_1 symmetry) took 63 iterations to converge to an error tolerance of 10^{-7} at 8.75 eV above the photoionization threshold. And the average number of iterations is 58 across our testing energy range in

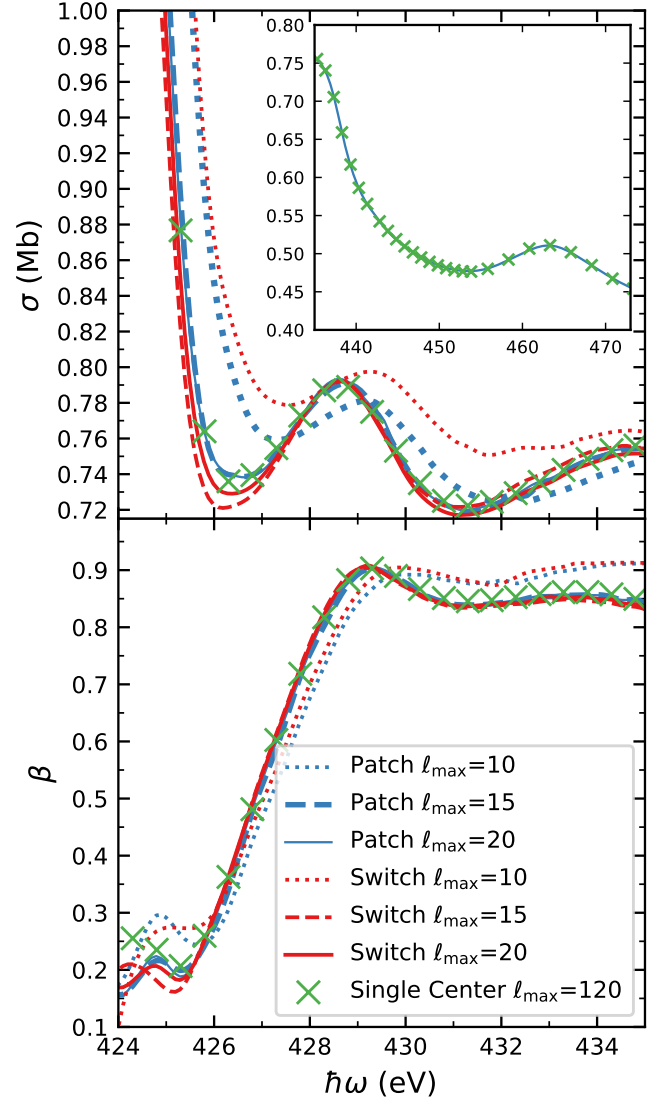


Figure 10: Convergence of the N(1s) photoionization cross section in the length gauge, σ_l , and the corresponding asymmetry parameter, β_L , for pyridine using the patch and switching-function algorithms and the single-center (SC) expanded Schwinger variational method within the static-exchange. The threshold energy is 423.3 eV.

A_1 symmetry.

Applying eq (26) to pyridine is not as simple as for the previous cases considered here. In pyridine there is more than one element at a range of distances from the origin. The average distance for the period 2 elements (C and N) is $r_{sg,0}=1.36 \text{ \AA}$ and the average distance to the period 1 element, i.e. H, is $r_{sg,0}=2.42 \text{ \AA}$. With an average subgrid radius of $0.6 \text{ \AA}$, the expected

converged $\ell_{cg,max}$ is then 15 including only the period 2 elements and 27 if the H atoms control $\ell_{cg,max}$.

Figure 10 compares the results for both the total cross section and the asymmetry parameter from the two overset-grid algorithms and the single-center expansion. The patch algorithm converges at $\ell_{cg,max}=15$, requiring no more partial waves than the much smaller example of CF_4 in Section 4.3. In pyridine, the value of $\ell_{cg,max}$ needed for convergence seems to depend on the location of the period 2 elements and not on the location of the H atoms. This might indicate that the value of the C_{Grid} depends on the period of the element. The switching function method is not converged at $\ell_{cg,max}=20$, this is particularly noticeable near the threshold at 423.3 eV (Koopmans’ theorem approximation). We were unable to completely converge the switching-function algorithm in this case near threshold. The single-center expansion with $\ell_{max} = 120$ using the Schwinger variational method gives results nearly identical to those of the converged overset grid methods, except for the asymmetry parameter near the threshold. The inset panel in Figure 10 shows the behavior of the patch algorithm at kinetic energies up to 50 eV. We see that the patch and single-center algorithms agree over the range of energies considered. This level of agreement indicates that the patch algorithm also yields accurate and stable results at high photoelectron kinetic energy. We note again that the convergence of the single-center expansion typically slows down near the converged limit, and so we were not able to completely converge that calculation to the benchmark accuracy of which it is in principle capable.

The plots in Figure 10 display a couple of salient features of pyridine nitrogen K-edge photoionization below 435 eV in the static-exchange approximation. First, there is a prominent π^* (1B_1 symmetry) shape resonance at a photon energy of about 428.8 eV (electron kinetic energy of 5.5 eV). Second, the photoionization cross section drops rapidly from threshold, while the asymmetry parameter rises rapidly. In this case, it is interesting to see the behavior of the angular distribution of the pho-

toelectron in the body frame where the physics of the photoionization process is most visible.

The development of experimental momentum imaging observations of ion fragments and electrons in coincidence has allowed the measurement of molecular frame photoelectron angular distributions (MFPAD).^{62,63} In particular, Williams et al.⁶⁴ and others observed that the fully differential cross section for photoionization, expressed in the molecular frame in eq (25), when averaged over the polarization directions, but still viewed in terms of photoelectron momentum in the molecular frame, reveals the tendency of the photoelectron to leave the molecule along or in between bonds, and thus reveals energy-dependent details of the photoejection process.

In Figure 11 we show the polarization-averaged MFPADs for N(1s) ionization of pyridine at several energies for which the total cross section is shown in Figure 10. The cross section is plotted as a surface with both its radial distance and color indicating the differential cross section for emission in that direction relative to the alignment of the molecule in space. Near threshold, the angular distribution is largely directed perpendicular to its principal symmetry axis (the axis connecting that nitrogen to the carbon opposite). However, as the photoelectron energy is swept through the resonance between 4.5 and 6.5 eV, an interesting and distinct feature emerges. The photoelectron is ejected away from the ring on the nitrogen side along the principal symmetry axis. Above the resonance energy, the polarization-averaged MFPAD returns to a more complicated pattern. The ability to calculate this level of detail efficiently and accurately in the photoionization of larger molecules, particularly in calculations with coupled electronic ionization channels, is the goal of the new algorithm we have presented here.

We have also used pyridine nitrogen K-edge photoionization to compare the speedup achieved using the patch versus the switching function method, shown in Table 3. The timings for the higher values of ℓ_{max}^{Switch} were estimated by an extrapolation for the wall-clock time for $\ell_{max}^{Switch} = 10$ to 25. The wall-clock

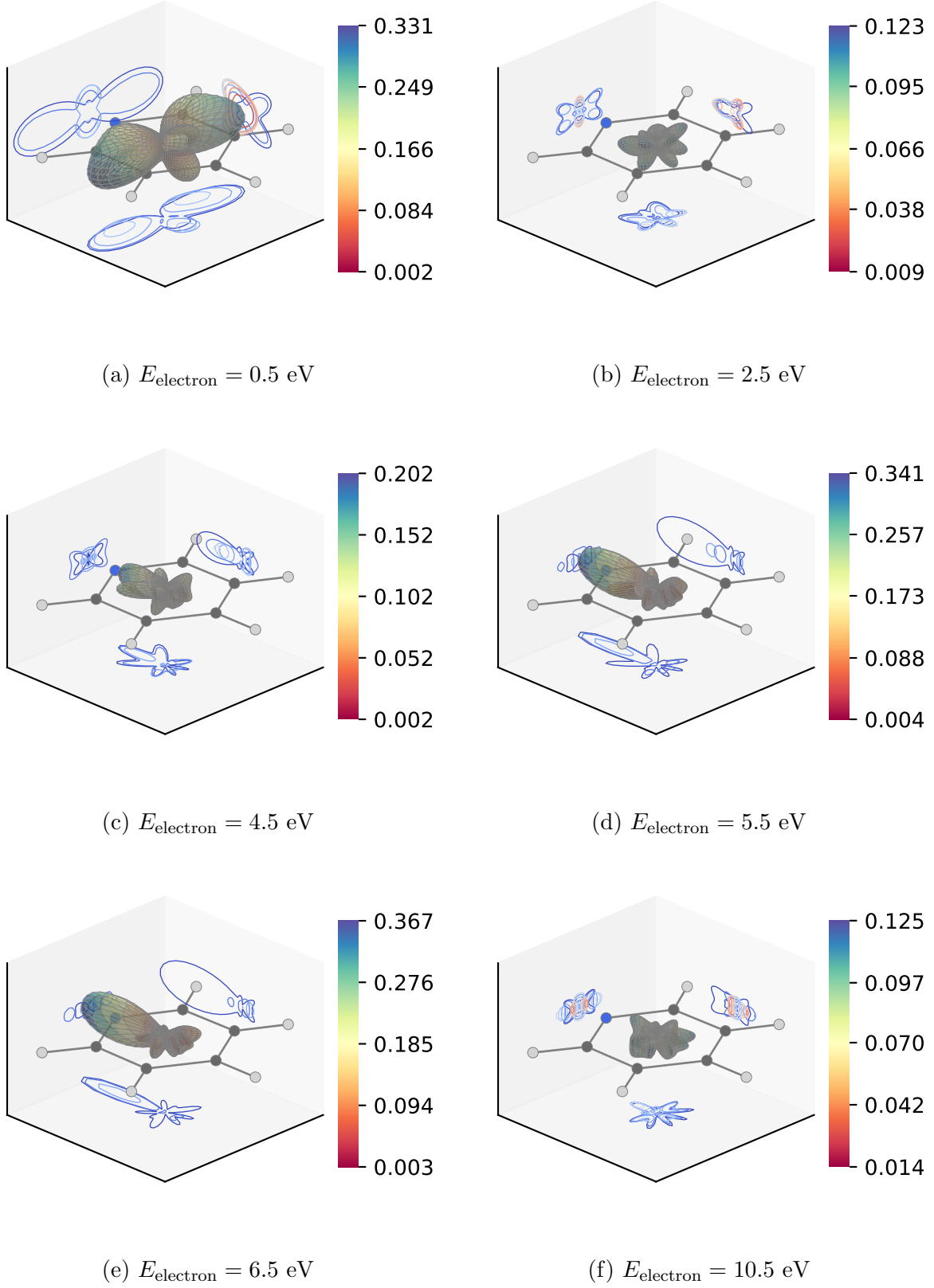


Figure 11: Polarization-averaged molecular-frame photoionization angular distributions for pyridine (nitrogen: blue, carbon: black, hydrogen: gray), calculated using the patch algorithm and $\ell_{cg,\text{max}}=15$ on the central grid. Each panel corresponds to a distinct photoelectron kinetic energy, as labeled. The π^* shape resonance in Figure 9 peaks near 5.5 eV corresponding to panel (d).

times using the same partial-wave expansion in the patch and switching function method were similar. However, comparing the converged partial-wave expansions times shows that the patch method is indeed faster, with speed-ups of more than a factor of six at the higher values of $\ell_{\max}$. Such higher value partial-wave expansions which will be needed for the study of larger molecular systems, i.e. for systems with higher values of $r_{sg,\max}$ as given in eq (26).

Table 3: Wall-clock speedup in **ePolyScat** using the patch method at a given $\ell_{\max}$ with the switch algorithm at $2\ell_{\max}$, which gives comparable accuracy. The values shown in parentheses are estimated using the switch algorithm execution times at lower values of $2\ell_{\max}$. All calculations are for the N(1s) photoionization of pyridine for the electron wave function with a_1 continuum symmetry at a photon energy of 425.8 eV.

$\ell_{\max}^{\text{Patch}}$	$\ell_{\max}^{\text{Switch}}$	$\frac{\text{Time Switch}}{\text{Time Patch}}$
10	20	2.4
15	30	(3.8)
20	40	(5.3)
25	50	(6.5)

5 Conclusion

In this work, we have presented a smooth overset-grid partitioning for the description of electron-scattering and photoionization wave functions that is rapidly convergent and scalable to large molecules. The increasing number of subgrids for systems with more atoms does not appreciably increase the number of angular momenta in the partial wave expansion on the central grid needed to achieve convergence. Increasing the size of the subgrids leads to more rapid convergence with respect to the partial wave expansion on the central grid. However, the size of the subgrids is limited by the requirement that the subgrids do not overlap. Overall, we see that the overset grid method overcomes the central limitation of the in-principle exact single-center expansion approach while retain-

ing all of the advantages of purely numerical grid methods.

The new algorithm outlined and thoroughly tested in the four computational examples presented here is now sufficiently robust for implementation in a general multichannel electron-scattering and photoionization procedure. The patch-algorithm version of the overset-grid approach provides the fundamental building block for such a capability. The most straightforward extension will be to include correlation through channel coupling and to use configuration interaction wave functions for the representation of the target states. Such an extension of a pure grid method has been made previously in our single-center expansion code for electron scattering from linear molecules.^{65,66} Furthermore, the underlying methodology is simple and can be readily adapted to other computational disciplines involving numerical multiple grid techniques.

Further study of the dependence of C_{Patch} on the periods of the elements in a molecule is needed to develop a general set of default parameters for the application of the patch algorithm. Such parameterization will be essential for a ready-to-use version of the program which we plan to make publicly available after further optimization, as has been done with the earlier version of **ePolyScat**.

Acknowledgement Work at LBNL was performed under the auspices of the US DOE under Contract DE-AC02-05CH11231 and was supported by the U.S. DOE Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division. Calculations presented here made use of the resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility, and the Lawrence computational cluster resource provided by the IT Division at the LBNL. Work at Kansas State University was supported by DOE, Office of Science, BES under Award DE-SC0022105.

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TOC Graphic

