CS 294 73 final project notes: Quantum Scattering

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These notes give the mathematical framework for single-photoionization in simple systems. This is the foundation for more interesting calculations that we may do.

I. FINITE-ELEMENT DISCRETE VARIABLE REPRESENTATION

The ECS tail introduces a discontinuity at R_0 and rather using *smoothing* techniques, we use finite-elements method (FEM) and set R_0 as one of the interval boundaries of a finite-element. In FEM, each independent variable r is replaced by a grid of nodes $0 \leq r_1 < r_2 < \cdots < r_N$, and a set of linearly independent local functions is used to represent the wave function in each interval. We assume the local basis functions are equal to one at the FEM boundary and zero outside of its element. We then subdivide the i'th interval into a set of n Gauss quadrature points x_m^i, $m = 1 \cdots n$. We use Gauss-Lobatto to approximate the integral

$$\int_{-1}^{1} g(x)dx \approx \sum_{m=1}^{n} g(x_m)w_m. \tag{1}$$

where the points and weights are chosen so that this equation is exact when $g(x)$ is a polynomial of degree $\leq 2n+1$. This equation can be generalized over an arbitary interval by the following scaling equations

$$\int_{r_i}^{r_{i+1}} g(x)dx \approx \sum_{m=1}^{n} g(x_m^i)w_m^i. \tag{2}$$

where

$$w_m^i = \frac{(r_{i+1} - r_i)}{2} w_m, \tag{3}$$

$$r_m^i = \frac{1}{2}[(r_{i+1} - r_i)x_m + (r_{i+1} + r_i)] \tag{4}$$

To construct a DVR based on Gauss-Lobatto quadrature, we choose the elementary basis to be a Lagrange interpolating polynomial called Lobatto shape functions:

$$f_{i,m}(x) = \begin{cases} \prod_{j \neq m} \frac{(x - x_j^i)}{(x_m^i - x_j^i)}, & r_i \leq x \leq r_{i+1} \\ 0, & x < r_i,\ x > r_{i+1} \end{cases} \tag{5}$$

To insure continuity of the wave function at the interval boundaries, we combine two shape functions from either side of the element boundary and create a *bridging* function, $\chi_{i,1}$:

$$\chi_{i,1}(x) = f_{i,n}(x) + f_{i+1,1}(x),$$
$$\chi_{i,m}(x) = f_{i,m}(x),\ m = 2, \ldots, n-1$$

Our basis is orthogonal and can be normalized by

$$\chi_{i,m}(x) \equiv f_{i,m}(x)/\sqrt{w_m^i},$$
$$\chi_{i,1}(x) \equiv \big(f_{i,n}(x) + f_{i+1,1}(x)\big)/\sqrt{w_n^i + w_1^{i+1}}$$

On the complex contour part of the FEM-DVR grid, the formalism is the same but just rotated by a complex exponential (see[1]).

II. SINGLE IONIZATION PROBLEM

If we have an initial state that is a solution to the Schödinger $H\Phi_0 = E\Phi_0$ with

$$H = \frac{1}{2}\nabla^2 + \frac{l(l+1)}{2\mu r^2} + V(r, Z) \tag{6}$$

where Z is the nuclear charge, then the scattering problem can be summed up into a simple $Ax = B$ equation:

$$(E_0 + \hbar\omega - H)\Psi^{sc} = \mu\Phi_0 \tag{7}$$

where μ is the dipole operator, and ω is the frequency of the photon. In our FEM-DVR grid, the potential is

$$\int_0^\infty f_{im}(x)V(x)f_{i'm'}(x)dx \approx \delta_{i,i'}\delta_{m,m'}V(x_m^i)w_m^i \tag{8}$$

and the kinetic energy matrix is given by

$$T_{m,m'}^{i,i'} \equiv \frac{1}{2}(\delta_{i,i'} + \delta_{i,i'+1}) \int_0^\infty dx \frac{d}{dx}\chi_{i,m}(x)\frac{d}{dx}\chi_{i',m'}(x) \tag{9}$$

with the delta functions reflecting the fact there are no overlap bewteen basis functions beyond adjacent intervals. The derivatives of the Lobatto functions are given by

$$f'_{im}(x'^i_m) = \begin{cases} \frac{1}{(x_m^i - x'^i_m)} \prod_{k \neq m,m'} \frac{(x'^i_m - x_k^i)}{(x_m^i - x_k^i)},\ m \neq m' \\ \frac{1}{2w_m^i}(\delta_{m,n} - \delta_{m,1}),\ m = m' \end{cases}$$

following Manolopoulus et al.(see[2]). With this representation of our Hamiltonian with a given potential V on the grid, we can solve the time-independent Schödinger equation for E_0 and Φ_0 using LAPACK zgeev. For z polorized light our dipole operator is

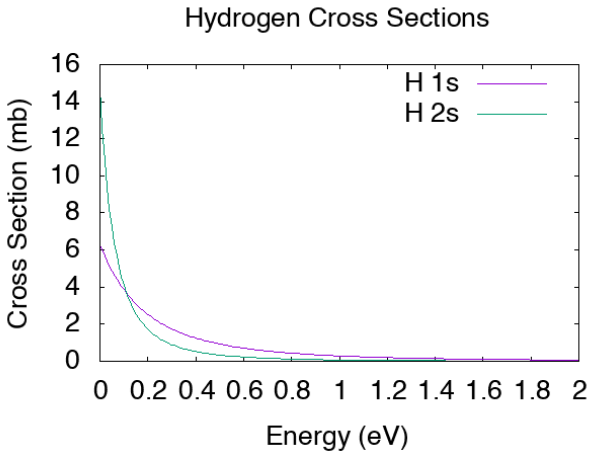
$$\mu = rY_1^0(\theta, \phi) = z\sqrt{\frac{3}{4\pi}}. \tag{10}$$

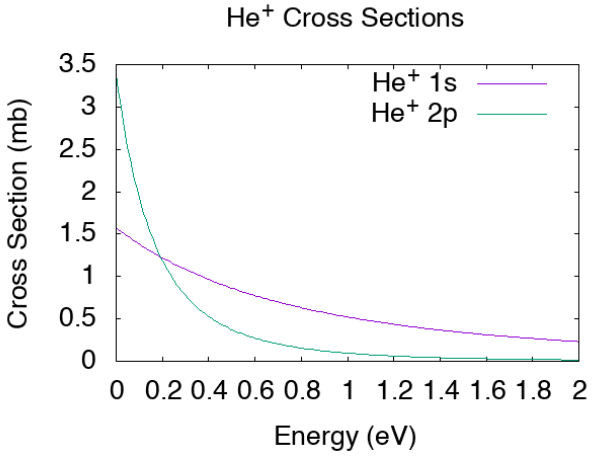
The angular part of our dipole matrix element is done analytically and the radial part which is just Φ_0 scaled by z. Now we are able to solve for Ψ^{sc} (i.e. x) in our driven equation using LAPACK zgesv. We can extract the probablity for the scattering event to occur (i.e. cross section) via the optical theorem

$$\sigma_{tot} = -\frac{8\pi}{k^2}\mathrm{Im} < \Psi^{sc}|\mu|\Phi_0 > . \tag{11}$$

III. SINGLE IONIZATION RESULTS

For our simple case with only one electron, we can look at many *hydrogen-like* atoms just by increasing the nuclear charge Z. Here are a few cross-sections that should be used as test cases. The orbitals we are ionizing from (e.g. $2s$) have analytic formulas that will be our right hand sides so the calculations are straight forward. The calculation for ionization from He^+ $2p$ orbital is slightly more complicated. A photon is a force carrying boson that has angular momentum $l = 1$ and as such the selection rules requires that our final state has $l = \pm 1$. Therefor we can transition from $P \rightarrow D$ (i.e. $+1$ transition) or $P \rightarrow S$ (i.e. -1 transition). Quantum mechanics dictates that both transitions occur with equal probability so the observed cross section will be the sum of these individual amplitudes.





IV. DOUBLE IONIZATION PROBLEM

Multi-electron problems present another difficulty because of the singularity of the electronic repulsion potential, $1/|r_i - r_j|$, in the Hamiltonian. In the single-center expansion basis, we define our three-dimensional basis functions as products of our FEM-DVR functions and spherical harmonics

$$\Phi_{ilm}(\boldsymbol{r}) = \phi_i(r) Y_{lm}(\theta, \phi). \tag{12}$$

The two-electron integrals we must compute are thus of the form

$$\left\langle \Phi_{il_1m_1}(\boldsymbol{r_1}) \Phi_{il_2m_2}(\boldsymbol{r_1}) \right| \frac{1}{|\boldsymbol{r_1} - \boldsymbol{r_2}|} \left| \Phi_{il_3m_3}(\boldsymbol{r_1}) \Phi_{il_4m_4}(\boldsymbol{r_1}) \right\rangle \tag{13}$$

where the integrations are over both electronic coordinates and are evaluated by making a multipole expansion of the interelectron repulsion

$$\frac{1}{|\boldsymbol{r_1} - \boldsymbol{r_2}|} = \sum_l \frac{r_<^l}{r_>^{l+1}} P_l(cos\theta_{12}). \tag{14}$$

The angular parts can be done analyitically and following [3] we have the radial part as

$$\begin{aligned} \left\langle \rho_B \right| \frac{r_<^l}{r_>^{l+1}} \left| \rho_A \right\rangle &= \left\langle \phi_j \phi_l \right| \frac{r_<^l}{r_>^{l+1}} \left| \phi_i \phi_k \right\rangle \\ &= \delta_{j,l} \delta i, k \Big(\frac{(2l+1)}{r_j \sqrt{w_j} r_i \sqrt{w_i}} \big[T_{j,i}^l \big]^{-1} + \frac{r_j^l r_i^l}{r_{mac}^{2l+1}} \Big) \end{aligned}$$

This is the final expression for the two-electron integrals in the FEM- DVR representation. With this machinery, we can find the scattering wavefunction for double-ionization from a multi-electron target.

V. CLASSES AND BRIEF DISCRIPTIONS

Lobatto Quadrature class

- Creates a wrapper to the Fortran routines and gives the user Lobatto points and weights.

Radau Quadrature class

- Creates a wrapper to the Fortran routines and gives the user Radau points and weights.

FEMDVR class

- Constructs a Finite-Element DVR grid with a complex Lauguerre-Radau quadrature tail. This uses the Radau boundaries $0 \rightarrow \infty$ that will mimic an infinite box better suited for time-dependent calculations. The constructor also puts the one-electron Hamiltonian and the inverse one-electron Hamiltonian on the grid saved as TXX and $TIXX$, respectively.
- There are getters for the points and the weights of the FEM-DVR grid. They maybe used elsewhere and in general it's nice to have.
- Plotting functions for the grid and wavefunctions for visual checking of grid and diagnolizing routines that generate the eigenfunctions.

- A symmetric member function is a good test to make sure the Hamiltonian is symmetric (i.e Hermitian). This will indicate that the bridging functions are correct.

- Getters for the other member data like R_0 maybe useful.

Dipole class

- Create various member functions for different polarization of light.

StaticPotential class

- This class creates various static potentials like square, yukawa, and coulomb.

Coul90 class

- This is a wrapper to call the Fortran.77 routines that computes a hypergeometric function like a coulomb wave, which are useful in scattering calculations.

- Has a member function that puts the Coulomb wavefunction on the DVR grid.

- Has a member function that generates the expansion coefficients of the coulomb wavefunction on the DVR grid.

- Has a plotting function for visual checking.

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[1] T. Rescingo and C. McCurdy, "Numerical grid methods for quantum-mechanical scattering problems," Physical Review A: Atomic, Molecular and Optical Physics **62**, 032706 (2000).

[2] D. E. Wyatt R. Manolopoulos, "Quantum scattering via the log derivative version of the khon variational principle," Chemical Physics Letters **152**, 23–32 (1988).

[3] M. Baertschy C. W. McCurdy and T. N. Rescigno, "Solving the three-body coulomb breakup problem using exterior complex scaling," Journal of Physics B: Atomic, Molecular, and Optical Physics **37**, 137–187 (2004).