

## Development of a Cartesian sinc DVR basis for single and double ionization

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# Molecular Hamiltonian

- Main goal is to solve  $\hat{H}\Psi = E\Psi$  for a general molecule
- We use a finite basis set defined on a Cartesian grid
- Non-relativistic Born-Oppenheimer approximation for Hamiltonian
- Assume atomic units:  $\hbar = m_e = 4\pi\epsilon_0 = a_0 = 1$

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_{i,a} \frac{Z_a}{|\vec{r}_i - \vec{R}_a|} + \sum_{i < j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

- $Z_a$  = nuclear charge
- $\vec{R}_a$  = nuclear coordinates
- $\vec{r}_i$  = electronic coordinates

# Grid Basis Properties

- Standard basis set methods can not represent electrons in the continuum
- Basis sets with  $N$  functions have  $O(N^4)$  two-electron matrix elements
- This is reduced to  $O(N^2)$  in a DVR grid basis
- Proven to work well on applications involving ionization
- Main drawback: basis set scales exponentially with number of electrons
- Hamiltonian matrix is very large and sparse which requires an iterative eigenvalue solver
- We develop a representation of the two-electron operator that only requires  $O(N)$  storage space and is exact on an infinite grid
- In progress: couple the grid basis with a molecular orbital basis to do problems involving single and double ionization of large molecules

# The Discrete Variable Representation (DVR)

- Potential matrix elements evaluated with numerical quadrature rules
- Integrals approximated as

$$\int_a^b f(x) dx \approx \sum_k w_k f(x_k)$$

- $x_k$  are the quadrature nodes and  $w_k$  are the weights
- Each node  $x_k$  has a corresponding basis function  $\chi_k(x)$
- A DVR basis has the property that  $\chi_i(x_j) = \delta_{ij} w_i^{-1/2}$
- Any local operator  $\hat{V}$  has a diagonal representation

$$\langle \chi_i | \hat{V} | \chi_j \rangle \approx \sum_k w_k \chi_i(x_k) V(x_k) \chi_j(x_k) = \delta_{ij} V(x_i)$$

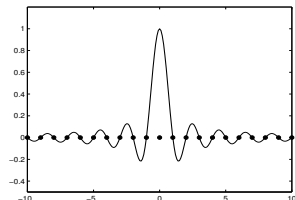
- DVR bases are always orthonormal with respect to the quadrature rule

$$\langle \chi_i | \chi_j \rangle \approx \sum_k w_k \chi_i(x_k) \chi_j(x_k) = \delta_{ij}$$

# Properties of the Sinc Basis

$$\chi_k(x) = \frac{1}{\sqrt{\Delta}} \operatorname{sinc}\left(\frac{x - x_k}{\Delta}\right)$$

$$\operatorname{sinc}(x) = \frac{\sin(\pi x)}{\pi x}$$



- The nodes are evenly spaced and centered around the origin

$$x_k = k\Delta, \quad k = -n, \dots, n, \quad N = 2n + 1$$

- The weights are all identical,  $w_k = \Delta$
- DVR-orthonormal and  $L^2$ -orthonormal
- Kinetic energy matrix elements are evaluated exactly

$$\langle \chi_i | \hat{T} | \chi_j \rangle = T_{ij} = \begin{cases} \pi^2 / (6\Delta^2) & \text{if } i = j \\ (-1)^{i-j} / (\Delta^2 (i-j)^2) & \text{if } i \neq j \end{cases}$$

- $T_{ij}$  only depends on  $i - j$ , i.e.  $T$  is a Toeplitz matrix
- 3D basis functions defined with 1D products

$$\chi_{ijk}(x, y, z) \equiv \chi_i(x) \chi_j(y) \chi_k(z)$$

# Coulomb Potential Matrix Elements

- The two-electron matrix elements:

$$[ij|kl] = \int \int d^3\vec{r}_1 d^3\vec{r}_2 \chi_i(\vec{r}_1) \chi_j(\vec{r}_1) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \chi_k(\vec{r}_2) \chi_l(\vec{r}_2)$$

- Define the functions

$$y^{kl}(\vec{r}_1) = \int d^3\vec{r}_2 \chi_k(\vec{r}_2) \chi_l(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|}$$

- Applying the Laplacian to both sides results in the Poisson equation

$$\nabla_{\vec{r}_1}^2 y^{kl}(\vec{r}_1) = -4\pi \chi_k(\vec{r}_1) \chi_l(\vec{r}_1)$$

- Expand  $y^{kl}$  in the DVR basis

$$y^{kl}(\vec{r}_1) \approx \sum_n y_n^{kl} \chi_n(\vec{r}_1)$$

- This results in the approximation

$$[ij|kl] = \frac{2\pi}{\sqrt{w_i w_k}} \delta_{ij} \delta_{kl} \mathbb{T}_{ik}^{-1}$$

- For a nucleus at grid point  $\vec{p}$ , the nuclear-electron attraction matrix elements are

$$y_{ii}(\vec{p}) = 2\pi w_i^{-1} \mathbb{T}_{ip}^{-1}$$

# $\mathbb{T}^{-1}$ Approximation

- Since  $\mathbb{T}$  is a Toeplitz matrix, it can be represented with only one index

$$\mathbb{T}_{ij} \rightarrow \mathbb{T}_{i-j}$$

- On an infinite grid, the same property would apply to  $\mathbb{T}^{-1}$ , which would satisfy

$$\mathbb{T} * \mathbb{T}^{-1} = \sum_{j=-\infty}^{\infty} \mathbb{T}_{i-j} \mathbb{T}_j^{-1} = \delta_{i0}$$

- $\mathbb{T}^{-1}$  can be thought of as a discretized Green's function for the operator  $\mathbb{T}$
- The Green's function for the exact operator  $\hat{\mathbb{T}}$  is

$$G(\vec{r}) = \frac{1}{2\pi|\vec{r}|}$$

- We expect that  $\mathbb{T}_i^{-1} \rightarrow G(\vec{r}_i)$  as  $|\vec{r}| \rightarrow \infty$
- Define  $\mathbb{T}^{-1}$  on a “big” grid that is at least twice the size of the computational grid
- Numerical strategy: Split  $\mathbb{T}^{-1}$  into an unknown short-range term  $Q$  and a long-range term using  $G(\vec{r})$

$$\mathbb{T}_i^{-1} = Q_i + G(\vec{r}_i), \quad -n_{big} \leq i \leq n_{big}$$

# $\mathbb{T}^{-1}$ Approximation (continued)

- Define an inner “small” box with  $N_{small}$  points per dimension
- The short range term  $Q$  is zero *outside* the small box
- The long-range term  $G$  is zero *inside* the small box

$$Q_i = \begin{cases} q_i & \text{if } \vec{r}_i \text{ in small box} \\ 0 & \text{otherwise} \end{cases}$$

$$G_i = \begin{cases} 0 & \text{if } \vec{r}_i \text{ in small box} \\ \frac{1}{2\pi|\vec{r}_i|} & \text{otherwise} \end{cases}$$

- This defines a system of  $N_{small}^3$  linear equations for  $q$

$$(\mathbb{T}q)_i = 2\pi\delta_{i0} - \Delta^3(\hat{\mathbb{T}}G)_i$$

- System is easily solved with a conjugate gradient method
- Must have  $n_{big} \geq 2n$  in order to evaluate  $\mathbb{T}_{i-j}^{-1}$  anywhere on the grid



# Hydrogen Calculations: DVR vs. Variational

The  $n = 1, 2$  eigenvalues and errors for hydrogen

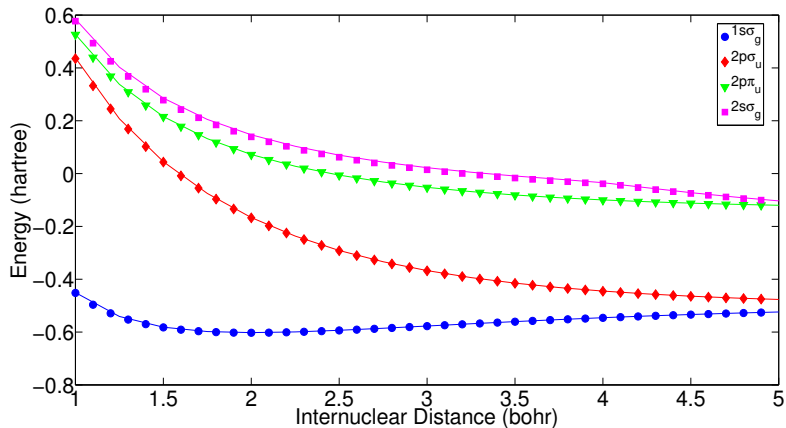
		DVR		Variational	
State	Exact	Computed	Abs. Error	Computed	Abs. Error
1s	-0.5	-0.4941	5.9E-3	-0.4881	1.2E-2
2s	-0.125	-0.1244	6.0E-4	-0.1206	4.4E-3
2p	-0.125	-0.1250	1.8E-5	-0.1238	1.2E-3

Virial theorem test for the  $n = 1, 2$  eigenvectors for hydrogen

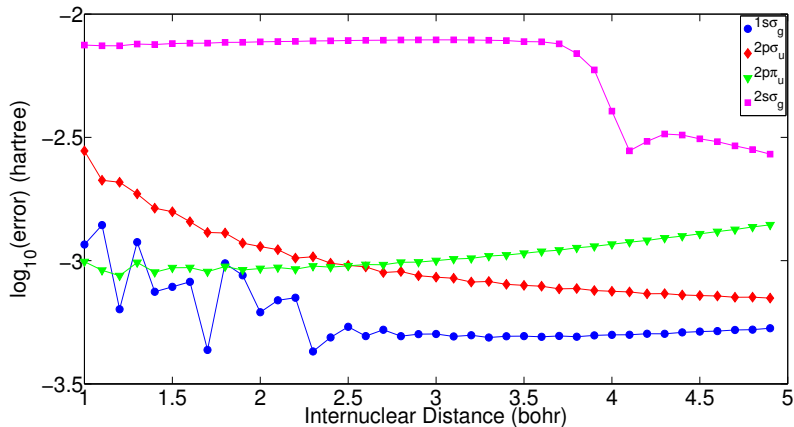
	DVR		Variational	
State	$\langle \hat{T} \rangle / \langle \hat{V} \rangle$	Abs. Error	$\langle \hat{T} \rangle / \langle \hat{V} \rangle$	Abs. Error
1s	−0.4939	6.0599E−3	−0.4817	1.8300E−2
2s	−0.4987	1.2724E−3	−0.5280	2.7996E−2
2p	−0.4998	2.2242E−4	−0.5184	1.8360E−2

Parameter values:  $N = 45$ ,  $\Delta = 0.4$

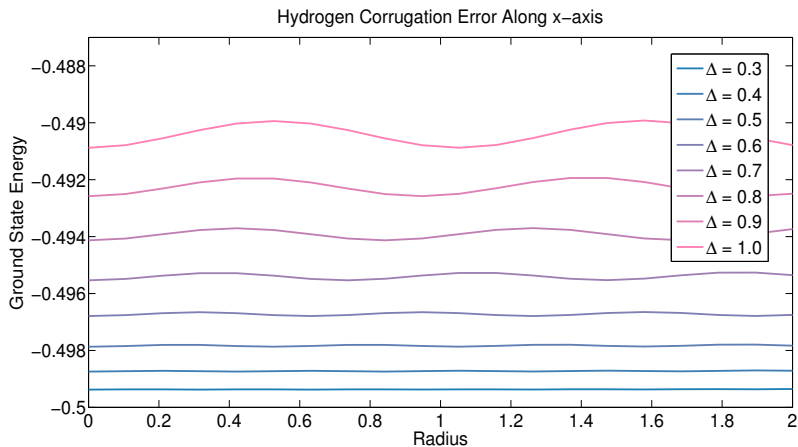
# $\text{H}_2^+$ Energy Curves



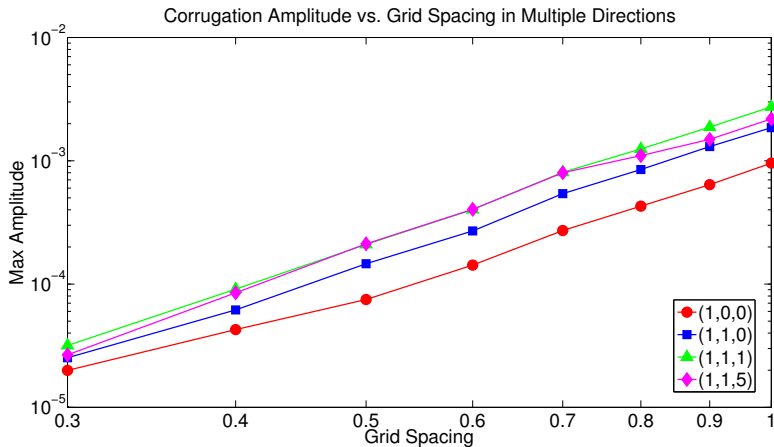
# Error in $\text{H}_2^+$ Energy Curves



# Hydrogen Energy vs. Radius



# Corrugation Amplitude vs. Grid Spacing



# Corrugation Amplitude Table

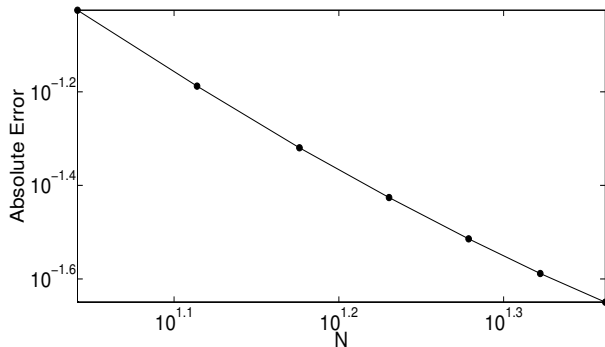
$\Delta$	(1, 0, 0)	(1, 1, 0)	(1, 1, 1)	(1, 1, 5)
0.3	1.9948e-5	2.5260e-5	3.1757e-5	2.6653e-5
0.4	4.2712e-5	6.1705e-5	9.0939e-5	8.4882e-5
0.5	7.4941e-5	1.4621e-4	2.0954e-4	2.1190e-4
0.6	1.4243e-4	2.6965e-4	4.0165e-4	4.0363e-4
0.7	2.7172e-4	5.4138e-4	8.0610e-4	8.0032e-4
0.8	4.2852e-4	8.4931e-4	1.2464e-3	1.1007e-3
0.9	6.4024e-4	1.3035e-3	1.8771e-3	1.4918e-3
1.0	9.5751e-4	1.8554e-3	2.7377e-3	2.1863e-3

**Table:** The maximum corrugation amplitude for the ground state energy of Hydrogen along different directions and for different grid resolutions with a fixed box size of 8 bohr.

# Helium Ground State

- Fixed box size  $[-3a_0, 3a_0]$  in each dimension
- Exact value to four digits:  $E_0 = -2.9037$
- Quadratic convergence rate observed

Convergence of Helium Ground State



$N$	$\Delta$	$E_0$
11	0.60	-2.8094
13	0.50	-2.8388
15	0.43	-2.8558
17	0.38	-2.8662
19	0.33	-2.8731
21	0.30	-2.8779
23	0.27	-2.8813

# Future Work

- Calculate metastable states of helium and lithium using the method of complex coordinate rotation
- Implement smooth exterior scaling with complex basis functions for arbitrary molecules
- Develop a hybrid basis of sinc DVR functions and molecular orbitals
- This will make ionization problems for many-electron systems practical
- Most electrons remain in orbitals with only one or two in the continuum