# A Sinc DVR Grid-Orbital Hybrid Basis for Electronic Structure


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## INTRODUCTION

- The main problem we wish to solve is to diagonalize a general molecular Hamiltonian with the non-relativistic Born-Oppenheimer approximation

$$\hat{H} = \hat{T} + \hat{V} = -\frac{1}{2}\sum_{i=1}^{N_e}\nabla_i^2 - \sum_{i=1}^{N_e}\sum_{k=1}^{N_{nuc}}\frac{Z_k}{|\mathbf{r}_i - \mathbf{R}_k|} + \sum_{i<j\leq N_e}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- Grid-orbital hybrid basis developed for single and double ionization applications
- Orbitals used to represent bound electrons and grid functions used to represent continuum electrons

## PRIMITIVE GRID BASIS

- The 1D grid is uniformly spaced with $2n+1$ points

$$x_j = j\Delta, \quad j = -n, ..., n, \quad x_j \in [-n\Delta, n\Delta]$$

- Expand the wave function in the $(2n+1)$-dimensional basis

$$\Psi(x) \approx \sum_{k=-n}^{n}\psi_k\tilde{\chi}_k(x),$$

$$\tilde{\chi}_k(x) = \frac{1}{\sqrt{\Delta}}\text{sinc}\left(\frac{x - x_k}{\Delta}\right), \quad \text{sinc}(x) = \frac{\sin(\pi x)}{\pi x}$$

- $L^2$ orthonormal: $\langle\tilde{\chi}_i|\tilde{\chi}_j\rangle = \delta_{ij}$
- DVR Property: $\tilde{\chi}_i(x_j) = \Delta^{-1/2}\delta_{ij}$
- Simple kinetic energy matrix elements known exactly

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

- Potential energy matrix representation is diagonal w.r.t. DVR quadrature

$$\langle\tilde{\chi}_i|\hat{V}|\tilde{\chi}_j\rangle \approx \sum_{k=-n}^{n}\Delta\tilde{\chi}_i(x_k)V(x_k)\tilde{\chi}_j(x_k) = \delta_{ij}V(x_i)$$

- 3D grid functions defined as products of 1D functions

$$\chi_{ijk}(\vec{r}) = \chi_i(x)\chi_j(y)\chi_k(z)$$

## PRIMITIVE HYBRID BASIS

- Let $M_1 = (2n+1)^3$ = dimension of the grid basis
- The one-electron hybrid basis consists of a set of $M_2 \ll M_1$ orthonormal orbitals expanded in the grid basis

$$\phi_\alpha(x) = \sum_{i=1}^{M_1}C_{i\alpha}\tilde{\chi}_i(x), \quad \alpha = 1, ..., M_2$$

and a set of modified grid functions defined as

$$\chi_i(x) = \sum_{j=1}^{M_1}Q_{ij}\tilde{\chi}_j(x), \quad i = 1, ..., M_1$$

- The matrix $Q = 1 - CC^T$ is chosen to ensure that every modified grid function is orthogonal to every orbital
- The hybrid basis $\mathcal{B}$ is defined by combining the modified grid functions and the orbitals

$$\mathcal{B} = \{\xi_1, ..., \xi_M\} = \{\chi_1, ..., \chi_{M_1}, \phi_1, ..., \phi_{M_2}\}, \quad M = M_1 + M_2$$

- Orbitals generated with Hartree-Fock method

## HYBRID BASIS MATRIX ELEMENTS

- Overlap matrix elements:

$$\langle\chi_i|\chi_j\rangle = Q_{ij}, \quad \langle\phi_\alpha|\phi_\beta\rangle = \delta_{\alpha\beta}, \quad \langle\chi_i|\phi_\alpha\rangle = 0$$

- Denote the one and two electron matrix elements of the primitive grid basis as

$$\tilde{h}_{ij} = \langle\tilde{\chi}_i|\hat{h}|\tilde{\chi}_j\rangle, \quad [\tilde{i}\tilde{j}|\tilde{k}\tilde{\ell}] = \delta_{ij}\delta_{k\ell}\tilde{V}_{ik}$$

- One-electron Hamiltonian matrix elements:

$$\begin{aligned}\langle\chi_i|\hat{h}|\chi_j\rangle &= \sum_{k,\ell}Q_{ik}Q_{j\ell}\langle\tilde{\chi}_k|\hat{h}|\tilde{\chi}_\ell\rangle = \sum_{k,\ell}Q_{ik}Q_{j\ell}\tilde{h}_{k\ell} \\ \langle\chi_i|\hat{h}|\phi_\alpha\rangle &= \sum_{k,\ell}Qik C_{\ell\alpha}\langle\tilde{\chi_k}|\hat{h}|\tilde{\chi}_\ell\rangle = \sum_{k,\ell}Q_{ik}C_{\ell\alpha}\tilde{h}_{k\ell} \\ \langle\phi_\alpha|\hat{h}|\phi_\beta\rangle &= \sum_{k,\ell}C_{k\alpha}C_{\ell\beta}\langle\tilde{\chi}_k|\hat{h}|\tilde{\chi}_\ell\rangle = \sum_{k,\ell}C_{k\alpha}C_{\ell\beta}\tilde{h}_{k\ell}.\end{aligned}$$

- Two-electron Hamiltonian matrix elements:

$$\begin{aligned}[ij|k\ell] &= \sum_{i'k'}Q_{ii'}Q_{jj'}Q_{kk'}Q_{\ell k'}\tilde{V}_{i'k'} \qquad [i\alpha|j\beta] = \sum_{i'k'}Q_{ii'}C_{i'\alpha}Q_{jk'}C_{k'\beta}\tilde{V}_{i'k'} \\ [ij|k\alpha] &= \sum_{i'k'}Q_{ii'}Q_{jj'}Q_{kk'}C_{k'\alpha}\tilde{V}_{i'k'} \qquad [i\alpha|\beta\gamma] = \sum_{i'k'}Q_{ii'}C_{i'\alpha}C_{k'\beta}C_{k'\gamma}\tilde{V}_{i'k'} \\ [ij|\alpha\beta] &= \sum_{i'k'}Q_{ii'}Q_{jj'}C_{k'\alpha}C_{k'\beta}\tilde{V}_{i'k'} \qquad [\alpha\beta|\gamma\delta] = \sum_{i'k'}C_{\alpha i'}C_{\beta i'}C_{\gamma k'}C_{\delta k'}\tilde{V}_{i'k'}\end{aligned}$$

## MULTI-ELECTRON BASIS

- The $N$-electron wave function is expanded in a basis of Slater determinants

$$\Psi(x_1, ..., x_N) = \sum_{\vec{m}}c_{\vec{m}}|\vec{m}\rangle$$

- The $M$ hybrid basis functions are used as the orbitals in the determinants

$$|\vec{m}\rangle = |\xi_{n_1}\cdots\xi_{n_N}\rangle, \quad 1 \leq n_i \leq M$$

- We only allow configurations with either 0,1 or 2 modified DVRs

$$\begin{aligned}|ij\vec{n}\rangle &\quad (2 \text{ modified DVRs, } N-2 \text{ orbitals}) \\ |i\vec{n}\rangle &\quad (1 \text{ modified DVR, } N-1 \text{ orbitals}) \\ |\vec{n}\rangle &\quad (0 \text{ modified DVRs, } N \text{ orbitals})\end{aligned}$$

- The $\vec{n}$ configurations are generated by taking single and double excitations of the Hartree-Fock configuration
- For single ionization applications, we do not include the determinants with two grid functions
- The overlap matrix has a block diagonal structure

$$\mathcal{S} = \begin{bmatrix}\langle ij\vec{n}|i'j'\vec{n}'\rangle & 0 & 0 \\ 0 & \langle i\vec{n}|i'\vec{n}'\rangle & 0 \\ 0 & 0 & \langle\vec{n}|\vec{n}'\rangle\end{bmatrix}, \qquad \begin{aligned}\langle ij\vec{n}|i'j'\vec{n}'\rangle &= \delta_{\vec{n}\vec{n}'}Q_{ii'}Q_{jj'} \\ \langle i\vec{n}|i'\vec{n}'\rangle &= \delta_{\vec{n}\vec{n}'}Q_{ii'} \\ \langle\vec{n}|\vec{n}'\rangle &= \delta_{\vec{n}\vec{n}'}\end{aligned}$$

- Since the basis functions are non-orthogonal, the typical Slater-Condon rules for Hamiltonian matrix elements do not apply and we develop a customized set of rules for determining these elements
- The method is made practical due to the low rank of the projector $P = CC^T$ and the fact that all orbitals are orthogonal to all grid functions

## HELIUM GROUND STATE

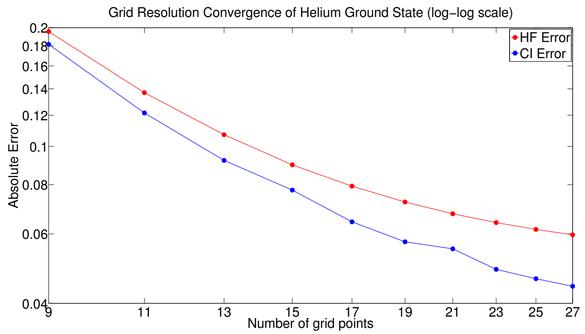


Figure: The absolute error in the calculated helium ground state energy for the Hartree-Fock method and the CI hybrid basis with one electron on the grid. The calculation used 8 spin orbitals and a fixed box size of 3 bohr.

## $H_2$ GROUND STATE

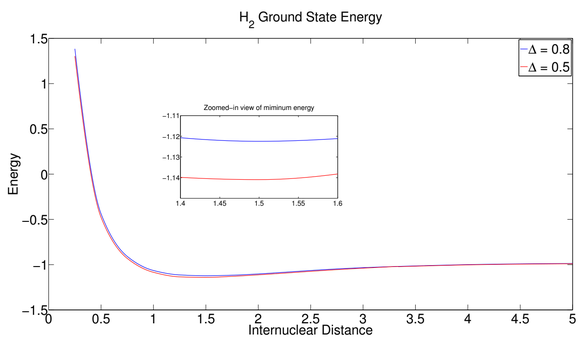


Figure: Ground state energy of $H_2$ vs. internuclear distance with one electron on the grid for $\Delta = 0.5, 0.8$ and using 8 spin orbitals.

## WORK IN PROGRESS

- Implement MCSCF method in the sinc DVR basis to obtain better orbitals
- Include 2 electrons on the grid for double-ionization applications
- Incorporate exterior complex scaling
- Implement a multi-resolution method, different grids for different orbitals