Discrete Variable Representation Introduction and Derivation

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1 Discrete Variable Representation

1.1 Introduction

Discrete Variable Representation (DVR) is an algorithmic approach to solving the time independent Schrodinger equation. It is a commonly used tool in the field of computational chemistry.

1.2 Basis functions

For DVR, a finite set of basis functions must be chosen. For this case our set $\{\phi_i\}_N$ belongs to a space such that they satisfy

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} \tag{1}$$

and thus are orthonormal. It follows that we can represent our wavefunction as

$$\psi = \sum_i c_i \phi_i \tag{2}$$

$$c_i = \langle \phi_i | \psi \rangle \tag{3}$$

1.3 Matrix Representations

Starting from the time independent Schrodinger equation

$$\hat{H}\psi = E\psi \tag{4}$$

recall that

$$\hat{H} = \hat{T} + \hat{V} \tag{5}$$

We want to represent our Hamiltonian as the sum of two matrices. Thanks to Colbert and Miller, the matrix elements of the kinetic energy matrix are analytically known.[1]

$$\hat{\mathbf{T}}_{ij} = \frac{\hbar^2(-1)^{i-j}}{2m\Delta x^2}\begin{cases}\frac{\pi^2}{3}, & i = j\\ \frac{2}{(i-j)^2}, & i \neq j\end{cases} \tag{6}$$

The potential at each point $V(x_i)$ must be evaluated using a potential energy surface for the system being studied. t follows that the potential energy matrix is diagonal.

$$\hat{\mathbf{V}}_{ij} = \delta_{ij}V(x_i) \tag{7}$$

Here the grid points x_i are evenly spaced by Δx and the size of the grid is appropriately large so that the wavefunction tends to zero at both ends. Doing so will represent an interval of $(-\infty, \infty)$. Now, we can add our kinetic and potential matrix representations together to get our Hamiltonian matrix.

$$\hat{\mathbf{H}} = \hat{\mathbf{T}} + \hat{\mathbf{V}} \tag{8}$$

1.4 Solving for ψ

Now all that remains is an eigenvalue problem.

$$\hat{\mathbf{H}}\psi = \epsilon_n\psi \tag{9}$$

$$(\hat{\mathbf{H}} - \epsilon_\lambda\mathbf{I})\psi = 0 \tag{10}$$

Nontrivial solutions exist when

$$det(\hat{\mathbf{H}} - \epsilon_\lambda\mathbf{I}) = 0 \tag{11}$$

which after solving provides us with our desired energy eigenvalues ϵ_n and thus their respected eigenvectors ψ.

2 References

[1] D. T. Colbert and W. H. Miller, J. Chem. Phys. 96, 1982 (1992).