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 Schrödinger 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 wave function 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 Schrödinger equation

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

recall that

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

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

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

It follows that the potential energy matrix is diagonal.

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

The potential at each point $V(x_i)$ must be evaluated using some form of a known potential energy surface for the system being studied. Here, the grid points x_i are evenly spaced by Δx and the size of the grid is appropriately large such that the wave function tends to zero at both ends. Doing so will represent the desired interval from $(-\infty, \infty)$. Now, the kinetic and potential energy matrix representations can be summed together to get our Hamiltonian matrix.

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

1.4 Solving for ψ

Substituting our Hamiltonian matrix representation into the Schrödinger equation, all that remains is an eigenvalue problem.

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

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

Nontrivial solutions exist when

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

which upon solving, provides the desired energy eigenvalues ϵ_n and their respected eigenvectors ψ.

2 References

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