Atomic Calculations using Finite Element DVR

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I. INTRODUCTION

The purpose of these notes is to outline a plan which uses the finite element discrete variable method(FEDVR) to perform atomic structure and scattering calculations. While any weight function is acceptable, here we restrict ourselves to the Legendre weight function, w(r)=1 and the points and weights of the Gauss-Legendre-Lobatto points mapped onto the domain of each element. Thus in each element, we have a set of DVR functions of the form,

$$\chi^i_{qlm}(r,\Omega) = Y_{lm}(\Omega)\psi^i_q(r) \tag{1}$$

where the set of points in interval i is required by the Lobatto rule to include the two endpoints. If the boundary conditions require it, either the first, last or both functions in a sub-interval may be absent from the basis. This is often necessary to satisfy the condition of regularity at the origin and decay of the bound-state wavefunctions at large radial distances. In order to connect up two adjacent regions, the last DVR function in region i and the first DVR function in region $i+1$ are linearly combined to get a bridge function,

$$\hat{\psi}^i_{n-1}(r) = \psi^i_n(r) + \psi^{i+1}_1(r). \tag{2}$$

Note that this function has a discontinuous derivative at the boundary which needs careful treatment. The collection of all of the bridge and non-bridge functions form the basis.

II. MATRIX ELEMENTS

A. one electron integrals

Since all of the integrals may be computed by integrating over the sub-domains and then summing the results, with the exception of integrals involving the derivatives of the bridge functions, all are straightforward. Since the kinetic energy operator contains a second derivative, it is necessary to "soften" the problem variationally by using Green's theorem (integration by parts) to get what is called, a variationally weak condition which avoids the non-existence of the second derivative at the boundary. This is functionally equivalent to modifying the second derivative by adding a Bloch operator in each interval. Thus we replace the radial kinetic energy operator in each interval by

$$L = -\frac{1}{2}\frac{d^2}{dr^2} + \frac{1}{2}\delta(r - r_{right})\frac{d}{dr} - \frac{1}{2}\delta(r - r_{left})\frac{d}{dr} \tag{3}$$

We now compute the required integrals. First the overlaps. For non-bridge functions,

$$O^{i,j}_{p,q} = \int dr \psi^i_p(r)\psi^i_q(r) = w^i_p \delta_{i,j}\delta_{p,q} \tag{4}$$

and for the bridge functions,

$$O^{i,i}_{n-1,n-1} = \int dr(\psi^i_n(r) + \psi^{i+1}_1(r))(\psi^i_n(r) + \psi^{i+1}_1(r)) = O^{i,i}_{n,n} + O^{i+1,i+1}_{1,1} = w^i_n + w^{i+1}_1 \tag{5}$$

So, all the overlaps are diagonal, as expected. Matrix elements involving any local potential, including the centrifugal potential, are also diagonal. Thus,

$$U^{i,j}_{p,q} = \int dr \psi^i_p(r)U(r)\psi^i_q(r) = w^i_p U(r^i_p)\delta_{i,j}\delta_{p,q} \tag{6}$$

and for the bridge functions,

$$U^{i,i}_{n-1,n-1} = \int dr(\psi^i_n(r)+\psi^{i+1}_1(r))U(r)(\psi^i_n(r)+\psi^{i+1}_1(r)) = U^{i,i}_{n,n}+U^{i+1,i+1}_{1,1} = (w^i_n+w^{i+1}_1)U(r^i_n) \tag{7}$$

Note that the normalization for the bridge functions removes the double weighting in the final normalized matrix elements. Now, turn to the L matrix elements. The non-bridge matrix elements are,

$$L^{i,i}_{p,q} = \int dr \psi^i_p(r)L\psi^i_q(r) = w^i_p \psi''^i_q(r^i_p) \tag{8}$$

The matrix elements between a non-bridge and bridge function are,

$$\begin{aligned} L^{i,i}_{p,n-1} &= \int dr \psi^i_p(r)L(\psi^i_n(r) + \psi^{i+1}_1(r)) \\ &= L^{i,i}_{p,n} \\ L^{i,i-1}_{p,m-1} &= \int dx \psi^i_p(r)L(\psi^i_1(r) + \psi^{i-1}_m(r)) \\ &= L^{i,i}_{p,1} \end{aligned} \tag{9}$$

Finally, the bridge-bridge matrix elements are,

$$\begin{aligned} L^{i,i}_{n-1,n-1} &= \int dr(\psi^i_n(r) + \psi^{i+1}_1(r))L(\psi^i_n(r) + \psi^{i+1}_1(r)) \\ &= L^{i,i}_{n,n} + L^{i+1,i+1}_{1,1} \\ L^{i,i-1}_{n-1,m-1} &= \int dr(\psi^i_n(r) + \psi^{i+1}_1(r))L(\psi^{i-1}_m(r) + \psi^i_1(r)) \\ &= L^{i,i}_{n,1} \end{aligned} \tag{10}$$

Thus, we see that there are never contributions to the matrix elements coming from cross interval integrations. Global matrix elements are simply formed from linear combinations

of matrix elements diagonal in the element indices. The entire calculation is simply reduced to computing,

$$\begin{aligned} L^{i,i}_{p,q} &= \int dr \psi^i_p(r) L(\psi^i_q(r) \\ &= \int_{r_{left}}^{r_{right}} dr \psi^i_p(r) L\psi^i_q(r) \end{aligned} \tag{11}$$

where we allow the indices p and q to be 1 and n. If we transform to the standard interval (-1,1), we get

$$L^{i,i}_{p,q} = -\frac{1}{r_{right}-r_{left}} \int_{-1}^{1} dr f \psi^i_p(x) \frac{d^2\psi^i_q(x)}{dx^2} + \frac{1}{2}\psi^i_p(1)\psi'^i_q(x) \mid_{x=1} -\frac{1}{2}\psi^i_p(-1)\psi'^i_q(x) \mid_{x=-1} \tag{12}$$

Clearly the surface terms vanish unless p is either 1 or n. For the remaining discussion, we assume we have re-normalized the FEDVR functions so that their INTEGRAL is unity.

B. two electron integrals

If we define atomic densities as the product of two of the orbitals, the two electron integrals may simply be written as,

$$V_{ij,kl} = \int d\mathbf{r_1} d\mathbf{r_2} \rho_{ik}(\mathbf{r_1}) \frac{1}{\mathbf{r_1}-\mathbf{r_2}} \rho_{jl}(\mathbf{r_2}) \tag{13}$$

Each of the densities is given as,

$$\rho_{ij}(\mathbf{r}) = \sum_{LM} d^{LM}_{l_i m_i l_j m_j} Y_{LM}(\Omega) \gamma_{ij}(r) \tag{14}$$

where the coupling of the spherical harmonics of the individual orbitals follows the usual Clebsch-Gordan rules. We may also expand the interaction potential in spherical harmonics,

$$\frac{1}{\mathbf{r_1}-\mathbf{r_2}} = 4\pi \sum_{lm} \frac{1}{(2l+1)} Y_{lm}(\Omega_1) Y_{lm}(\Omega_2) \frac{r^l_<}{r^{l+1}_>} \tag{15}$$

The two electron integral may then be reduced to,

$$\begin{aligned} V_{ij,kn} = 4\pi \sum_{LM} \frac{1}{(2L+1)} d^{LM}_{l_i m_i l_k m_k} d^{LM}_{l_j m_j l_n m_n} \int r_1^2 dr_1 r_2^2 dr_2 \gamma_{ik}(r_1) \frac{r^L_<}{r^{L+1}_>} \gamma_{jn}(r_2) \\ = 4\pi \sum_{LM} \frac{1}{(2L+1)} d^{LM}_{l_i m_i l_k m_k} d^{LM}_{l_j m_j l_n m_n} V^L_{ij,kl} \end{aligned} \tag{16}$$

The essential difficulty with this integral is the derivative discontinuity of the radial matrix element. A naive application of the quadrature rule relating the DVR functions to simple

sums over the values of functions at the quadrature points, yields poor accuracy. However, it is possible to avoid this and to retain high accuracy by using Poisson's equation. We define

$$U^L_{ik}(r) = \int r_1^2 dr_1 \gamma_{ik}(r_1) \frac{r_<^L}{r_>^{L+1}} \tag{17}$$

which is equivalent to the radial differential equation,

$$\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}U^L_{ik}(r) - \frac{L(L+1)}{r^2}U^L_{ik}(r) = -(2L+1)\gamma_{ik}(r) \tag{18}$$

In writing this I assume that the orbitals are defined to behave as r^{l+1} at the origin, so that the radial density is actually the product of two orbitals divided by r^2 This has the effect of cancelling a factor of $\frac{1}{r^2}$ from both sides of the above equation.

$$\frac{d}{dr}r^2\frac{d}{dr}U^L_{ik}(r) - L(L+1)U^L_{ik}(r) = -(2L+1)\psi^t_i(r)\psi^v_k(r) \tag{19}$$

We now define,

$$U^L_{ik}(r) = \frac{V^L_{ik}(r)}{r} \tag{20}$$

to get,

$$\frac{d^2}{dr^2}V^L_{ik}(r) - \frac{L(L+1)}{r^2}V^L_{ik}(r) = -(2L+1)\frac{\psi^t_i(r)\psi^v_k(r)}{r} \tag{21}$$

To solve this differential equation requires two boundary conditions. These can be discovered by looking at the definition of U^L,

$$U^L_{ik}(r) = \frac{1}{r^{L+1}}\int_0^r dr_1 \psi^t_i(r_1)\psi^v_k(r_1) r_1^L + r^L \int_r^{r_N} dr_1 \frac{\psi^t_i(r_1)\psi^v_k(r_1)}{r^{L+1}} \tag{22}$$

At $r = 0$, U^L behaves like r^L and the multiplicative r factor which converts to V^L, gives a zero boundary condition at the origin for all L. At the last point, U^L behaves like $\frac{1}{r^{L+1}}$ and the multiplicative r factor gives,

$$V^L_{ik}(r_N) = \frac{1}{r_N^L}\int_0^\infty dr \psi^t_i(r)\psi^v_k(r) r^L = \frac{r_i^L}{r_N^L}\delta_{i,k} \tag{23}$$

This extremely simple result is a consequence of the use of the DVR basis. So, now we may solve eq(21). The simplest formal procedure is to solve the differential equation for a solution which is zero at both boundaries and to then add a solution of the homogeneous equation satisfying the inhomogeneous boundary condition at the last point.

$$V^L_{ik}(r) = \sum_{j\neq N} c^{ik}_j \psi_j(r) + r^{L+1}\frac{r_i^L}{r_N^{2L+1}}\delta_{i,k} \tag{24}$$

Note that the last DVR function is excluded from the sum to ensure a zero value at the last point. Inserting the expression about into equation(21) and projecting onto the basis yields,

$$\sum_t T_{it} c_t^{jl} = -(2L+1)\delta_{i,j}\delta_{j,l}\frac{1}{\sqrt{w_i} r_i} \tag{25}$$

The matrix T is defined as,

$$T_{ij} = \langle \psi_i \mid \frac{d^2}{dr^2} - \frac{L(L+1)}{r^2} \mid \psi_j \rangle \tag{26}$$

and the integration must be performed using the Bloch operator for the second derivative. The formal solution to this equation is,

$$c_i^{jl} = -(2L+1) T_{ij}^{-1} \delta_{j,l} \frac{1}{\sqrt{w_j} r_j} \tag{27}$$

Using this yields the final expression for U_{jl}^L

$$U_{jl}^L(r) = -(2L+1)\frac{\delta_{j,l}}{r r_j \sqrt{w_j}} \sum_i T_{ij}^{-1} \psi_i(r) + \delta_{j,l} \frac{r^L r_j^L}{r_N^{2L+1}} \tag{28}$$

and therefore,

$$V_{ij,kl}^L = \delta_{i,k}\delta_{j,l}\big[-(2L+1)\frac{T_{ij}^{-1}}{r_i\sqrt{w_i} r_j \sqrt{w_j}} + \frac{r_i^L r_j^L}{r_N^{2L+1}}\big] \tag{29}$$

III. HAMILTONIAN

The next step in the process is the construction of the Hamiltonian matrix from the one-and-two-electron integrals. Since there is nothing physical about the FEDVR basis, a first step, would be to set up some model, single particle Hamiltonian, preferably with a local but realistic interaction, and diagonalize it to get a single set of orbitals. It would be possible to use the Fock Hamiltonian but that would require using the two-electron integrals. Not impossible, but perhaps more than is needed.

So, initially, we set up a one-body problem using the FEDVR. Let us consider the structure of the one-body Hamiltonian matrix for two finite elements with 3 basis functions in the first and 2 in the second element.

$$\begin{pmatrix} (H_{1,1}-E) & H_{1,2} & 0 & 0 & 0 \\ H_{2,1} & (H_{2,2}-E) & H_{2,3} & 0 & 0 \\ 0 & H_{3,2} & (H_{3,3}-E) & H_{3,4} & 0 \\ 0 & 0 & H_{4,3} & (H_{4,4}-E) & H_{4,5} \\ 0 & 0 & 0 & H_{5,4} & (H_{5,5}-E) \end{pmatrix}$$

If we were to consider the first element as an "internal" region, where exchange and correlation effects were important and the second element as an "external" region, dominated by long-range forces, the connection is provided by the "bridge" function which straddles the two regions. A reasonable approach would be ignore region two and just diagonalize the leading (3x3) submatrix to get a set of "internal" orbitals. These orbitals would be used to build the many-electron spin-eigenfunctions required for the target states and the pseudostates.