Variation Method

Variation principle

$\frac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau} \geq E_1$, where ϕ is any well-behaved function that satisfies the boundary conditions of the problem. This is because the wavefunction ϕ can be expanded in the basis set of the eigenfunctions of the problem, i.e. $\phi = \sum_k a_k \psi_k$

To get the higher states

Remove ψ_1 from the summation, i.e. $\phi = \sum_{k=2}^{\infty} a_k \psi_k$. This can be ensured only if the trial wavefunction is orthogonal to the ground state eigenfunction, $\langle \psi_1 | \phi \rangle = 0$. This is quite difficult except in certain cases e.g. when alternate eigenfunctions are odd/even.

Determinants

Minor, Cofactor,

Diagonal, Block diagonal

Simultaneous Linear Equations

$$a_{11}x_1 + a_{12}x_2 + \cdots + a_{1n}x_n = b_1$$

$$a_{21}x_1 + a_{22}x_2 + \cdots + a_{2n}x_n = b_2$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$a_{n1}x_1 + a_{n2}x_2 + \cdots + a_{nn}x_n = b_n$$

If at least one of the $b's$ is not equal to zero, we have a system of **inhomogeneous** linear equations. One could use the Cramer's rule to solve it.

$$x_k = \frac{\begin{vmatrix} a_{11}\ a_{12} \ldots a_{1,k-1}\ b_1\ a_{1,k+1} \ldots a_{1n} \\ a_{21}\ a_{22} \ldots a_{2,k-1}\ b_2\ a_{2,k+1} \ldots a_{2n} \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ a_{n1}\ a_{n2} \ldots a_{n,k-1}\ b_n\ a_{n,k+1} \ldots a_{nn} \end{vmatrix}}{\det(a_{ij})}, \qquad k = 1, 2, \ldots, n$$

Gaussian Elimination

1) Divide 1st equation by a_{11}: Makes coefficient of x_1 unity
2) Subtract a_{21} times the 1st equation from the 2nd equation. Similarly do for the rest of the equations. Now the coefficients of x_1 are zero for all the equation except the first.

3) Repeat the above steps taking nth equation and dividing it by a_{nn}. Subtract only the equations below the nth equation.
4) This gives a triangular form with the last equation having only the x_n term equal to the RHS.
5) Substitute back and get the values of all x_i.
6) If all the equations are subtracted instead of only the equations below the nth equation, we get a diagonal form of the equations and the solutions can be read straightaway. This is known as the **Gauss-Jordan elimination** method. However, it is slower than Gaussian elimination.

Linear Homogeneous equations

If all the b's are zeros

Trivial solution $x_1 = x_2 = \cdots = x_n = 0$ when $\det(a_{ij}) \neq 0$

When $\det(a_{ij}) = 0$ the solution is non-trivial

If a solution exists, $x_k = d_k$, then $x_k = cd_k$ is also a solution. Therefore, the solution contains an arbitrary constant and determination of the absolute values of the unknowns is impossible. Let us choose $x_n = c$ and transfer the last term of each equation to the RHS.

$$a_{11}x_1 + a_{12}x_2 + \cdots + a_{1,n-1}x_{n-1} = -a_{1,n}c$$

$$a_{21}x_1 + a_{22}x_2 + \cdots + a_{2,n-1}x_{n-1} = -a_{2,n}c$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$a_{n-1,1}x_1 + a_{n-1,2}x_2 + \cdots + a_{n-1,n-1}x_{n-1} = -a_{n-1,n}c$$

$$a_{n1}x_1 + a_{n2}x_2 + \cdots + a_{n,n-1}x_{n-1} = -a_{n,n}c$$

Now we have n equations and $n-1$ unknowns. Discard any one equation and solve it as a linear inhomogeneous equation. The form of the solution will be $x_1 = ce_1, x_2 = ce_2, \ldots, x_{n-1} = ce_{n-1}, x_n = c$

The procedure fails when the $n-1$ equation system still remains homogeneous. What to do? Introduce another constant!

Linear Variation Functions

Trial wavefunction: $\phi = c_1f_1 + c_2f_2 + \cdots + c_nf_n = \sum_{j=1}^{n} c_jf_j$

c_j: parameters to be determined by minimizing the variational integral, f_j: basis functions

$$\int \phi^* \phi \, d\tau = \int \sum_{j=1}^{n} c_j f_j \sum_{k=1}^{n} c_k f_k \ d\tau = \sum_{j=1}^{n} \sum_{k=1}^{n} c_j c_k \int f_j f_k \, d\tau$$

Overlap integral $S_{jk} = \int f_j f_k \, d\tau$

Numerator: $\int \phi^* \hat{H} \phi \, d\tau = \sum_{j=1}^{n} \sum_{k=1}^{n} c_j c_k \int f_j \hat{H} f_k \, d\tau$, where $H_{jk} = \int f_j^* \hat{H} f_k \, d\tau$

This gives the variational integral: $W \sum_{j=1}^{n} \sum_{k=1}^{n} c_j c_k \, S_{jk} = \sum_{j=1}^{n} \sum_{k=1}^{n} c_j c_k \, H_{jk}$

Minimize $W(c_1, c_2, \ldots, c_n)$ w.r.t. c_i's. $\frac{\partial W}{\partial c_i} = 0$

$$\frac{\partial W}{\partial c_i} \sum_{j=1}^{n} \sum_{k=1}^{n} c_j c_k \, S_{jk} + W \frac{\partial}{\partial c_i} \sum_{j=1}^{n} \sum_{k=1}^{n} c_j c_k \, S_{jk} = \frac{\partial}{\partial c_i} \sum_{j=1}^{n} \sum_{k=1}^{n} c_j c_k \, H_{jk}, \qquad i = 1,2,3 \ldots, n$$

Since c_j's are independent variables, $\frac{\partial c_j}{\partial c_i} = \delta_{ij}$

implies, $\frac{\partial}{\partial c_i} \sum_{j=1}^{n} \sum_{k=1}^{n} c_j c_k \, S_{jk} = \sum_{k=1}^{n} \sum_{j=1}^{n} c_k \, \delta_{ij} S_{jk} + \sum_{j=1}^{n} \sum_{k=1}^{n} c_j \delta_{ik} S_{jk} = \sum_{k=1}^{n} c_k S_{ik} + \sum_{j=1}^{n} c_j S_{ji}$

Real functions. Therefore $S_{ji} = S_{ij}^* = S_{ij}$. So above expression is, $2 \sum_{k=1}^{n} c_k S_{ik}$

Similarly, $\frac{\partial}{\partial c_i} \sum_{j=1}^{n} \sum_{k=1}^{n} c_j c_k \, H_{jk} = 2 \sum_{k=1}^{n} c_k H_{ik}$

$$2W \sum_{k=1}^{n} c_k S_{ik} = 2 \sum_{k=1}^{n} c_k H_{ik}$$

$$\sum_{k=1}^{n} [(H_{ik} - S_{ik} W) c_k] = 0, \qquad i = 1, 2, 3 \ldots, n$$

We have a set of simultaneous, linear, homogeneous equations in the n unknowns $c_1, c_2, \ldots, c_n$. This is known as a **secular equation**. This gives rise to the secular determinant.

$$\begin{vmatrix} H_{11} - S_{11}W & H_{12} - S_{12}W & \ldots & H_{1n} - S_{1n}W \\ H_{21} - S_{21}W & H_{22} - S_{22}W & \ldots & H_{2n} - S_{2n}W \\ & \ldots & & \\ & \ldots & & \\ H_{n1} - S_{n1}W & H_{n2} - S_{n2}W & \ldots & H_{nn} - S_{nn}W \end{vmatrix} = 0$$

This gives n roots $W_1 \leq W_2 \leq \cdots \leq W_n$

The bound states of the system are in the order $E_1 \leq E_2 \leq \cdots \leq E_n$

Then (MacDonald's proof) $E_1 \leq W_1, \quad E_2 \leq W_2, \quad E_3 \leq W_3$ ….

Get one value of W. Solve for c_i's. Get the eigenfunction corresponding to this W.

Want more eigenvalues, use more basis funtions.

Want more accuracy, use more basis functions.

Matrices

Inverse: $A^{-1}A = AA^{-1} = 1$

Symmetric: $a_{ij} = a_{ji}$

Hermitian: $d_{ij} = d_{ij}^*$ (Note: all symmetric matrices need not be Hermitian)

Transponse: A^T is the matrix formed by interchanging the rows and columns of A. $a_{ij}^T = a_{ji}$

Complex conjugate: $A^* : a_{ij}^*$

Conjugate transpose: $A^\dagger = (A^*)^T$: $a_{ij}^\dagger = a_{ji}^*$

Orthogonal matrix: $A^{-1} = A^T$

Unitary matrix: $U^{-1} = U^\dagger$

If the $S_{ij} = \delta_{ij}$ in the set of n-homogeneous linear equations, i.e. the f_k's are orthonormal, then we can write

$$\boldsymbol{HC} = \boldsymbol{CW}$$

Which gives, $C^{-1}HC = W$

The problem is then to diagonalize H.

Hückel MO theory

Case of ethane: sp^2 sigma bonded framework + π orbitals

$$\psi_\pi = c_1 2p_{zA} + c_2 2p_{zB}$$

Secular determinant

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

Hückel proposed: $S_{ij} = \delta_{ij}$, All Coulomb integrals (H_{ii}) are the same.

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

Gives, $E = \alpha \pm \beta$

α approximates the energy of the electron in an isolated $2p_z$ orbital. It can be used as a reference point for the zero of energy. β is determined experimentally and has a value of -75 kJ mol^{-1}.