**Approximate Methods in Quantum Chemistry**
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**Lecture No. 34**
**Evaluation of Molecular Properties**

Hello students! Welcome to this lecture. In the last lecture we discussed the non-linear solution of the Hartree-Fock-Roothan equations. In this lecture, we will look at how we can evaluate molecular properties.

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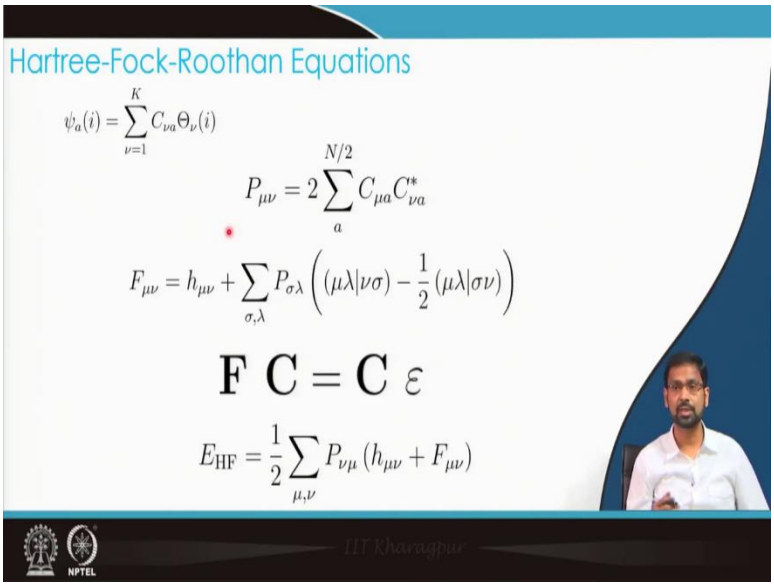


The HF-Roothan scheme involves the solution of the following eigenvalue problem,

$$\mathbf{F}\ \mathbf{C} = \mathbf{C}\ \varepsilon$$

Where the Fock matrix is given by

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\sigma,\lambda} P_{\sigma\lambda}\left((\mu\lambda|\nu\sigma) - \frac{1}{2}(\mu\lambda|\sigma\nu)\right)$$

The Fock matrix depends on the 1-electron core-Hamiltonian matrix, the 2-electron (4-center) integrals, and the density matrix (**P**), whose elements are given by

$$P_{\mu\nu} = 2\sum_{a}^{N/2} C_{\mu a}C^*_{\nu a}$$

Where $C_{\nu a}$ are the matrix elements of the expansion coefficient matrix that defines a spatial orbital ($\psi_a$) in terms of the basis functions $\{\Theta_\nu\}$ by $\psi_a(i) = \sum_{\nu=1}^{K} C_{\nu a}\Theta_\nu(i)$

Once the density matrix, the Fock matrix, and the core-Hamiltonian matrix are known, the HF energy can be obtained by

$$E_{\mathrm{HF}} = \frac{1}{2}\sum_{\mu,\nu} P_{\nu\mu}\left(h_{\mu\nu} + F_{\mu\nu}\right)$$

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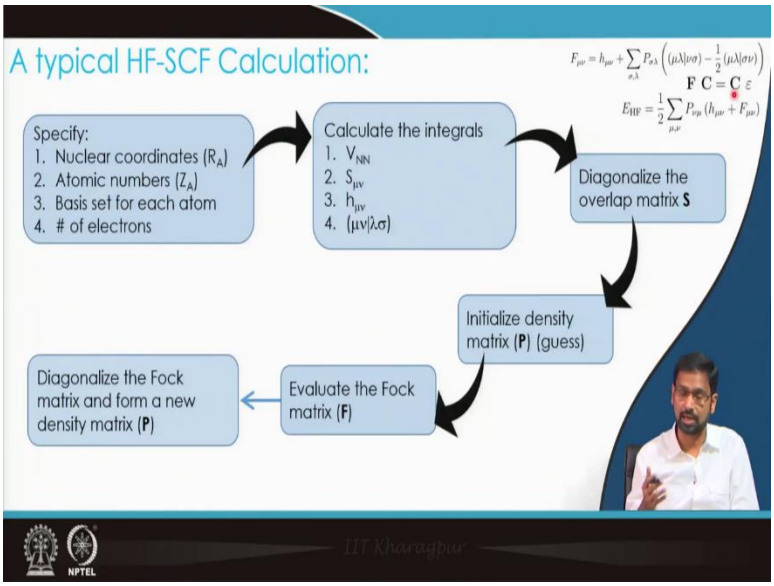


With the above set of results, let us now discuss the algorithm of a typical HF-SCF calculation.

For a molecule of choice, we need to specify the nuclear coordinates, the atomic numbers of the constituent atoms, the total number of electrons in the molecule (we can define a cationic/anionic system by changing the number of electrons) and the spin-multiplicity of the state of interest. For each atom in a molecule, we define a set of basis functions (we still have not discussed, what kind of basis functions to use. We will discuss this in a later lecture). These are the initial requirements (or the input for HF calculation) based on the problem at hand. Next, we will try to solve the SCF problem within Born-Oppenheimer approximation (i.e., the electronic problem will be solved for a fixed nuclear arrangement).

Next, we evaluate all the integrals. Based on nuclear positions, we can obtain $V_{\mathrm{NN}}$ (the nuclear repulsion energy constant). The next task is to evaluate the one-electron Hamiltonian matrix elements ($h_{\mu\nu}$). These one-electron integrals are rather easy to evaluate. The most time-consuming part of the integral evaluation is the two-electron integrals which appear in the Coulomb and exchange parts of the Fock matrix. It is a

common practice to calculate all the integrals, store them in a computer and then use them as and when required. When working with a real molecule, the molecular symmetry (if any), helps reduce the computational cost. From the basis functions, we can calculate the overlap matrix elements. Note that these basis functions are over different nuclei, and hence these matrix elements will depend on the nuclear arrangement.

Next, we initialize the density matrix by an initial guess. One way is to start the initial guess for the density matrix as a null-matrix (0-matrix). In that case, the Fock matrix is essentially the core-Hamiltonian matrix, with no interelectronic interactions. Since the solution will be obtained iteratively, in subsequent iterations the 2-electron terms would start making contribution. Instead of using a null matrix, it is a common practice to use some empirical information for the initial guess of the density matrix. It is customary to use (extended) Hückel matrix concept to generate the initial guess for the density matrix.

Once the density matrix is initialized, the Fock matrix can be computed easily (remember, all integrals are precomputed) and then diagonalized to obtain the expansion coefficient matrix (from the eigenvectors). These expansion coefficient matrix elements are used to form the new density matrix, which in turn is used to generate the new Fock matrix. This process is iterated till convergence. Note, diagonalization of large matrix is a routine computational process that can be achieved with small effort.

The convergence is tested against some predefined criteria. For example, the change in the density matrix between two iterations must be less than a threshold. The value of the threshold determines the accuracy and also the cost. Alternatively, the HF energy can be used as a metric for convergence. For each SCF iteration, with the help of one-electron matrix, density matrix and Fock matrix, the HF energy can be calculated. The convergence criteria can be set as, when the change in the HF energy between two consecutive steps is less than some predefined value, say $10^{-6}$ Hartree.

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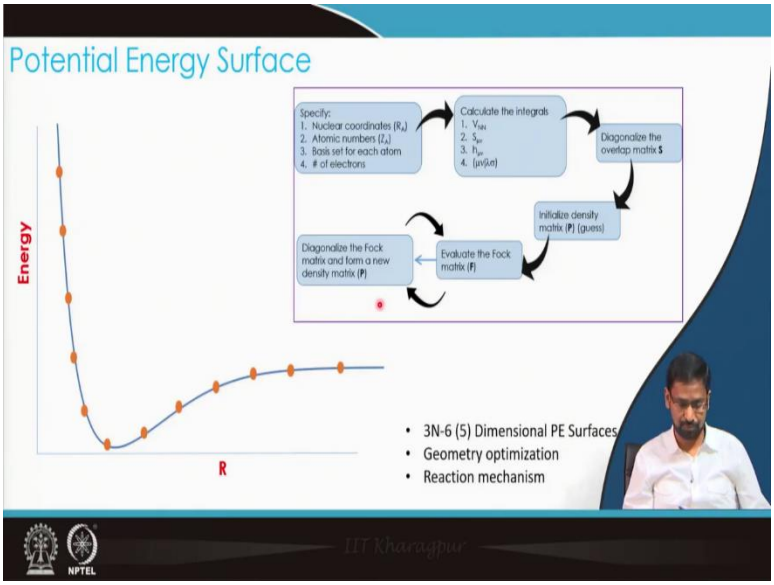


During the above-described procedure we kept the geometry fixed. The electronic part of the problem was solved with fixed nuclear arrangement. For a different nuclear arrangement, the entire process needs to be repeated, as the values of the integrals would change when atomic positions change (note: the basis functions are centered on the nuclear positions). For a diatomic molecule, there is only one internal coordinate, i.e., the internuclear distance ($R$). When we carry out the HF-SCF calculations for a range of $R$ values, we get a different energy for each value of $R$. When we connect these points in the energy-vs-distance diagram, we obtain a potential-energy curve. For an $N$-atomic (non-linear) molecule, there are $3N$-6 number of internal degrees of freedom. Hence, by varying geometry along each internal degree of freedom, we can construct a $3N$-6 dimensional potential-energy surface.

Using a similar strategy, we can find out a particular nuclear configuration in the $3N$-6 dimensional PE surface which corresponds to the lowest potential energy. That geometry is called the optimized geometry, or the most probable geometry of the molecule. Not only that, we can now compare the energies of a set of reactants and that of the resulting products to determine the reaction energy and even reaction mechanism. The Hartree-Fock procedure, therefore, plays a central role in computational chemistry with its applications in obtaining information about chemical processes.

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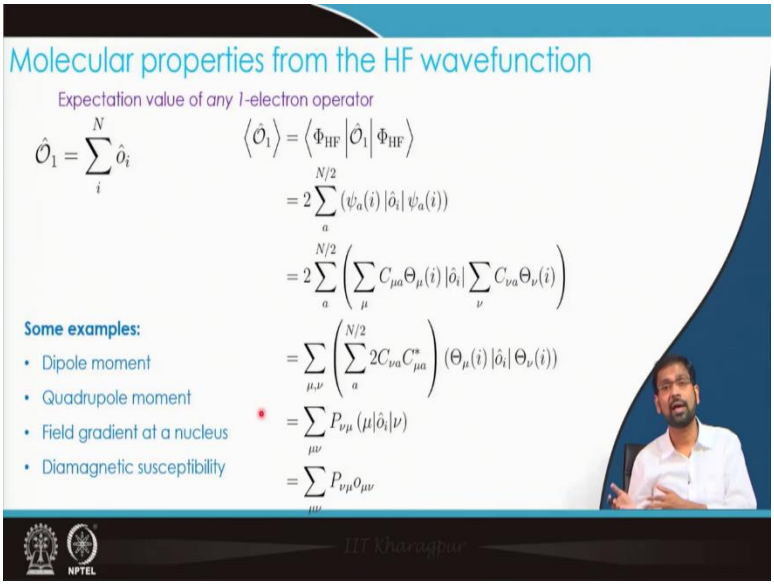


So far, from HF method we have obtained only the energy. Apart from energy, there are other molecular properties that we are also interested in. Some of these molecular properties depend on the quantum mechanical operators that depend only on one electron or sum of one-electron operators, for example, the dipole moment, the quadruple moment, the field gradient at a nucleus, the diamagnetic susceptibility and many other. No matter which properties they are, if we know that a classical observable corresponds to a quantum mechanical operator which depends on one electron at a time, we can evaluate the corresponding properties in the following way. Let us define an operator as a sum of N-number of 1-electron operators

$$\hat{\mathcal{O}}_1 = \sum_i^N \hat{o}_i$$

The expectation value of this operator when the state is defined as the Slater determinant obtained from the HF orbitals is given by,

$$\begin{aligned}
\left\langle \hat{\mathcal{O}}_1 \right\rangle &= \left\langle \Phi_{\mathrm{HF}} \left| \hat{\mathcal{O}}_1 \right| \Phi_{\mathrm{HF}} \right\rangle \\
&= 2 \sum_{a}^{N/2} \left( \psi_a(i) \left| \hat{o}_i \right| \psi_a(i) \right) \\
&= 2 \sum_{a}^{N/2} \left( \sum_{\mu} C_{\mu a} \Theta_\mu(i) \left| \hat{o}_i \right| \sum_{\nu} C_{\nu a} \Theta_\nu(i) \right) \\
&= \sum_{\mu,\nu} \left( \sum_{a}^{N/2} 2 C_{\nu a} C_{\mu a}^{*} \right) \left( \Theta_\mu(i) \left| \hat{o}_i \right| \Theta_\nu(i) \right) \\
&= \sum_{\mu\nu} P_{\nu\mu} \left( \mu | \hat{o}_i | \nu \right) \\
&= \sum_{\mu\nu} P_{\nu\mu} o_{\mu\nu}
\end{aligned}$$

For the 2nd line of the above equation, recall our earlier discussion on obtaining the expectation value of a 1-electron operator when the wave function is given by a Salter determinant. In the third line the orbitals are expressed as a linear combination of basis functions, and in the fifth line the definition of density matrix is used.

From the above equation, the expectation value of any one-electron operator requires two quantities: the density matrix (which is available at the end of the HF calculation) and the only other quantity that needs to be evaluated is the one-electron operator matrix ($o_{\mu\nu}$) in terms of the basis functions.

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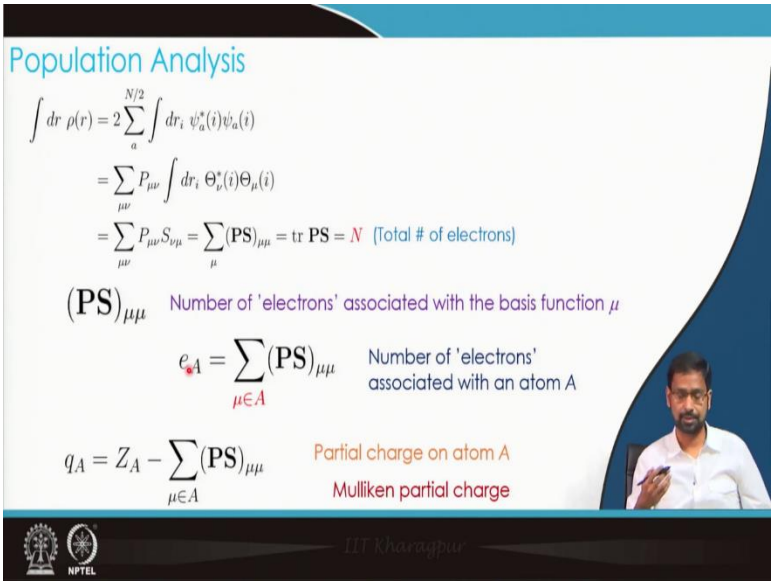


Now let us discuss population analysis. For an *N*-electron system, $\int dr\ \rho(r)$ represents the total charge density. We can evaluate it as,

$$\int dr\ \rho(r) = 2\sum_{a}^{N/2}\int dr_i\ \psi_a^*(i)\psi_a(i)$$
$$= \sum_{\mu\nu} P_{\mu\nu}\int dr_i\ \Theta_\nu^*(i)\Theta_\mu(i)$$
$$= \sum_{\mu\nu} P_{\mu\nu}S_{\nu\mu} = \sum_{\mu}(\mathbf{PS})_{\mu\mu} = \mathrm{tr}\ \mathbf{PS} = N$$

The above equation tells that the trace of the **PS** matrix is equivalent to total electronic charge (*N*). If sum of all $(\mathbf{PS})_{\mu\mu}$ is the total number of electron *N*, the individual value of $(\mathbf{PS})_{\mu\mu}$ is the 'number of electrons' associated with the basis function μ. Each basis function is centred on an atom. If we collect all the basis functions $\mu$ on an atom *A*, and find the sum of $(\mathbf{PS})_{\mu\mu}$, we would get the 'number of electrons' associated with atom *A*, i.e.,

$$e_A = \sum_{\mu\in A}(\mathbf{PS})_{\mu\mu}$$

The partial charge of this atom can be obtained by adding the nuclear charge of the atom $Z_A$ with the electronic charge, i.e., $q_A = Z_A - \sum_{\mu\in A}(\mathbf{PS})_{\mu\mu}$

The partial charge on an atom in a molecule obtained from the above described way is known as the Mulliken charge. Please note that there is no unique way of separating the overall charge density on a molecule into its atomic components. Mulliken population analysis is one of the most straightforward way of evaluating partial charges.

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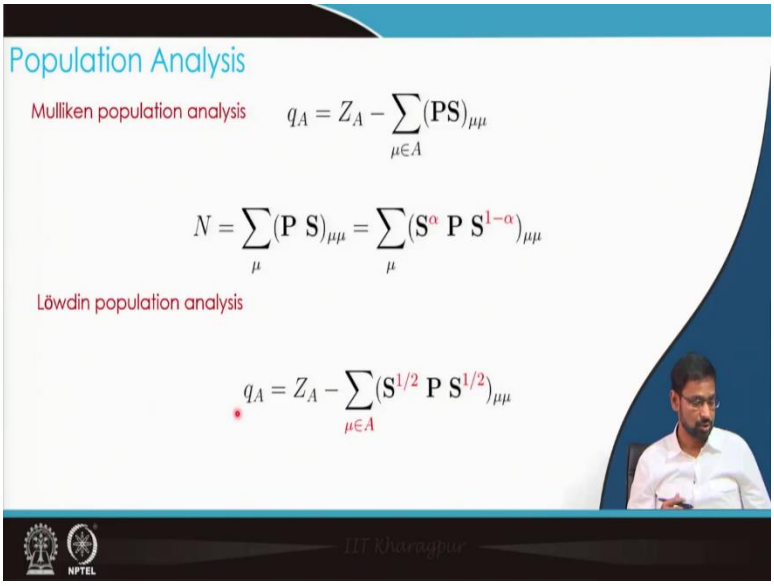


In Mulliken population analysis we considered the trace of the **PS** matrix. We can also express it in the following way,

$$N = \sum_{\mu} (\mathbf{P}\ \mathbf{S})_{\mu\mu} = \sum_{\mu} (\mathbf{S}^{\alpha}\ \mathbf{P}\ \mathbf{S}^{1-\alpha})_{\mu\mu}$$

Where, α can take any value between 0 and 1. For a special (symmetric) case of $\alpha = 1/2$, the partial charge on an atom in a molecule can be expressed as,

$$q_A = Z_A - \sum_{\mu \in A} (\mathbf{S}^{1/2}\ \mathbf{P}\ \mathbf{S}^{1/2})_{\mu\mu}$$

The partial charges obtained from the above relation are called the Löwdin charges.

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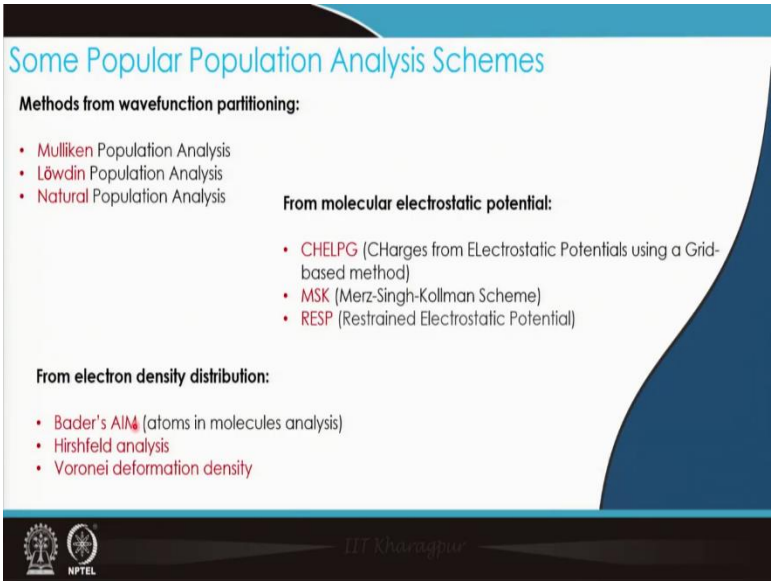


Apart from Mulliken and Löwdin charges, there are other methods for obtaining partial charges. Some of the popular population analysis methods are listed above in the slide. There are several other strategies, e.g., decomposition of the molecular electrostatic potentials, and the electron density distribution, that are popularly used for population analysis.

Thank you for your attention.