Basic Quantum Procedures

The following issues have been discussed in class.

Classical Mechanics and the Langrange and Hamilton formulation.
Classical and Quantum mechanics from Feynman path integral. QuantumPostulates.
Relation to uncertainty relations.
Units

$$\frac{\hbar^2}{m} = 7.62 \text{ eV} \cdot \mathring{A}^2$$

$$e^2 = 14.4 \text{ eV} \cdot \mathring{A}^2$$

States in a Box and in a Ring: Boundary conditions Quantization.
Oscillation Theorem. Evaluation through the Poincaré transformation.
Density of states.
Separation of variables. Convolution.
Variational procedure. The case of the Hydrogen atom.
Radial equation for a central potential. Angular and radial Quantum numbers. Spherical Harmonics. Hydrogen atom.
The discrete Schrödinger equation. Evaluation through the Promotion matrix.
Perturbation theory.
Stark effect in an excited hydrogen atom. or in a Lithium atom. The hybrid sp orbitals. Cristalline field.

Two coupled states

There is only one calculation that we will do in this course, the solution of a 2×2 matrix of the form

$$\mathbf{H} = \begin{bmatrix} E_1 & V_{12} \\ V_{21} & E_2 \end{bmatrix}$$

of course we know that the eigenvalues are obtained from

$$\det[\varepsilon \mathbf{I} - \mathbf{H}] = (\varepsilon - E_2)(\varepsilon - E_1) - V_{12}V_{21} = 0$$

as:

$$\varepsilon_{\pm} = \frac{E_2 + E_1}{2} \pm \sqrt{\left[\frac{E_2 - E_1}{2}\right]^2 + V_{12}V_{21}}$$

$$= \tfrac{1}{2}[E_2 + E_1 \pm \hbar\omega^{(1)}]$$

since

$$\hbar\omega^{(1)} = \sqrt{\left[\frac{E_2 - E_1}{2}\right]^2 + V_{12}V_{21}} \geq 0$$

the election of the **lower sign** corresponds to the **ground state**, i.e. $\varepsilon_+ \geq \varepsilon_-$.

The election of the eigenvectos requires somewhat more work. In Landau-Lifshitz p.140 they are written as

$$c_{1\pm} = \langle 1|\pm\rangle = \sqrt{\frac{V_{12}}{|V_{12}|}}\left[\frac{1}{2}\left(1 \mp \frac{E_2 - E_1}{\hbar\omega^{(1)}}\right)\right]^{1/2}$$

$$c_{2\pm} = \langle 2|\pm\rangle = \pm\sqrt{\frac{V_{21}}{|V_{12}|}}\left[\frac{1}{2}\left(1 \pm \frac{E_2 - E_1}{\hbar\omega^{(1)}}\right)\right]^{1/2}$$

Notice the following: The term in the square bracket is positive. In general, for an hermitian Hamiltionian $V_{12} = |V|\exp[i\phi]$ and $V_{21} = |V|\exp[-i\phi]$ hence the prefactor can be is the positive square root of a complex number.

For example, let us consider the usual situation where $E_2 = E_1$ and $V_{12} = -V$. Hence, the **ground** state has the coefficients i and $\pm(-i) = i$ respectively indicating the eigenstate has is a **symmetric** combination of previous states

$$|-\rangle = i\frac{1}{\sqrt{2}}[|1\rangle + |2\rangle].$$

In contrary the excited state has the coefficients i and $-i$ and hence is an antisymmetric combination

$$|+\rangle = i\frac{1}{\sqrt{2}}[|1\rangle - |2\rangle].$$

Of course the purely real combinations would work equally well.

We will do it with some detail bellow because it will serve to refresh the linear algebra procedures.

Unitary transformations

Let us consider a real Hamiltonian writen in term of the orthonormal basis:

$$\hat{e}_1 = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \text{ and } \hat{e}_2 = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

which has the form:

$$\mathbf{H} = \begin{bmatrix} E_1 & V_{12} \\ V_{21} & E_2 \end{bmatrix}$$

The non-diagonal terms implies that our old eigenvectors are mixed by a perturbation and in we have to find a new basis. We know that the eigenvectors of the form which are of course orthornormal can be writen in terms of the old basis

$$\hat{s}_1 = \begin{bmatrix} \cos\theta \\ \sin\theta \end{bmatrix} \quad \text{and} \quad \hat{s}_2 = \begin{bmatrix} -\sin\theta \\ \cos\theta \end{bmatrix}$$

The matriz that transforms a vector in the **new** basis **into** its component of the **old** one is then a diagonal form has to be a rotation matrix:

$$\mathbf{U}^{-1} = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix}$$

This transformation takes a vector in the **new** basis and transforms it **into** the **old** basis. The columns are the eigen-vectors of the Hamiltonian.

Analogousy its inverse

$$\mathbf{U} = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix} = [\mathbf{U}^{-1}]^{-1}$$

which takes a vector a vector expressed writen in the **old** basis and represents it **into** the **new** one. Notice the property $\mathbf{U}^{-1} = (\mathbf{U}^*)^t \equiv \mathbf{U}^\dagger$. The dagger symbol, $\dagger$, indicates that one has to take complex conjugate of each element indicated by the $*$ symbol and then transpose it, ie. exchange files from rows.

Therefore, the new diagonal representation the Hamiltonian is

$$\underbrace{\mathbf{H}'}_{\text{new diag. repres.}} = \underbrace{\mathbf{U}}_{\text{new}\leftarrow\text{old}} \cdot \underbrace{\mathbf{H}}_{\text{old non-diag.}} \cdot \underbrace{\mathbf{U}^\dagger}_{\text{old}\leftarrow\text{new}}$$

or

$$\underbrace{\mathbf{H}}_{\text{old non-diag. repres.}} = \underbrace{\mathbf{U}^\dagger}_{\text{old}\leftarrow\text{new}} \cdot \underbrace{\mathbf{H}'}_{\text{new diag.}} \cdot \underbrace{\mathbf{U}}_{\text{new}\leftarrow\text{old}}$$

Let us consider the equation that one would get from the first eigenvector, the eigenvalue equation $\mathbf{H}\hat{s}_1 = \varepsilon\,\hat{s}_1$

$$\begin{cases} E_1\cos\theta & +V_{12}\sin\theta & = & \varepsilon\cos\theta \\ V_{21}\sin\theta & +E_2\sin\theta & = & \varepsilon\sin\theta \end{cases}$$

which is rewitten as

$$\begin{cases} V_{12}\sin\theta & = (\varepsilon - E_1)\cos\theta & \rightarrow & \mathrm{tg}\theta = \dfrac{V_{12}}{\varepsilon - E_1} \\ (\varepsilon - E_2)\cos\theta & = V_{21}\sin\theta & \rightarrow & \mathrm{tg}\theta = \dfrac{\varepsilon - E_2}{V_{21}} \end{cases}$$

$$\begin{cases} \mathrm{tg}^2\theta = \dfrac{1-\cos^2\theta}{\cos^2\theta} = \dfrac{(V_{12})^2}{(\varepsilon-E_1)^2} \\[4mm] \mathrm{tg}^2\theta = \dfrac{\sin^2\theta}{1-\sin^2\theta} = \dfrac{(\varepsilon-E_2)^2}{(V_{21})^2} \end{cases}$$

from which:

$$\begin{cases} 1-\cos^2\theta = \cos^2\theta\,\dfrac{(V_{12})^2}{(\varepsilon-E_1)^2} \\[4mm] \sin^2\theta = (1-\sin^2\theta)\,\dfrac{(\varepsilon-E_2)^2}{(V_{21})^2} \end{cases}$$

here we recognize that the fraction terms can be obtained from the descriminant equation which can be squared to obtain:

$$\frac{|V_{12}|^2}{(\varepsilon-E_1)^2} = \frac{(\varepsilon-E_1)^2}{|V_{12}|^2}$$

hence replacing

$$1-\cos^2\theta+\sin^2\theta = \left[(1-\sin^2\theta+\cos^2\theta)\frac{|V_{12}|^2 e^{i2\phi}}{(\varepsilon-E_1)^2}\right]$$

$$1-\cos 2\theta = (1+\cos 2\theta)\frac{|V_{12}|^2}{(\varepsilon-E_1)^2}$$

$$\cos 2\theta\left[\frac{|V_{12}|^2}{(\varepsilon-E_1)^2}+1\right] = 1-\frac{|V_{12}|^2}{(\varepsilon-E_1)^2}$$

finally

$$\cos\theta = \frac{1-\dfrac{|V_{12}|^2}{(\varepsilon-E_1)^2}}{1+\dfrac{|V_{12}|^2}{(\varepsilon-E_1)^2}} = \frac{(\varepsilon-E_1)^2-|V_{12}|^2}{(\varepsilon-E_1)^2+|V_{12}|^2}$$

$$\cos 2\theta = \frac{(\varepsilon-E_1)\dfrac{|V_{12}|^2}{(\varepsilon-E_2)}-|V_{12}|^2}{(\varepsilon-E_1)\dfrac{|V_{12}|^2}{(\varepsilon-E_2)}+|V_{12}|^2} = \frac{\dfrac{(\varepsilon-E_1)}{(\varepsilon-E_2)}-1}{\dfrac{(\varepsilon-E_1)}{(\varepsilon-E_2)}+1}$$

$$= \frac{E_2-E_1}{2\varepsilon-E_2-E_1}$$

to analize the denomitator we are going to use again the expresion for the eigenvalues

$$2\varepsilon - E_2 - E_1 = 2\left[\frac{E_2 + E_1}{2}\right]$$

$$= \pm\sqrt{(E_2 - E_1)^2 + 4|V_{12}|^2}$$

$$= \pm\hbar\omega^{(1)}$$

The last equality is just a definition, whose physical meaning will became apparent further on, which now simplifies the notation

$$\cos 2\theta = \frac{E_2 - E_1}{\pm\hbar\omega^{(1)}}$$

now

$$\cos\theta = \sqrt{\frac{1+\cos 2\theta}{2}}$$

$$\sin\theta = \sqrt{\frac{1-\cos 2\theta}{2}}$$

Hence the eigenvectors components are

$$\cos\theta = \left\{\frac{1}{2}\left[1 + \frac{E_2 - E_1}{\hbar\omega^{(1)}}\right]\right\}^{1/2}$$

$$\sin\theta = \left\{\frac{1}{2}\left[1 - \frac{E_2 - E_1}{\hbar\omega^{(1)}}\right]\right\}^{1/2}$$

finally we migth want to write the full expression of the new eigenvectors. Here, I was not able to keep track of the phase of the interaction term properly. I need help to improve the above calculation.

Electrons in a box once more.

We learned to solve a box with hard wall boundary condition as well as the problem of periodic boundary conditions. The first thing we want to point out is that tight binding models, although naturally associated with Linear Combination of Atomic Orbitals (LCAO) can also be obtained as a convenient approximation to the Schrödinger equation written in terms of the continuous coordinate x :

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x) + U(x)\psi(x) = \varepsilon\psi(x)$$ #

where $U(x)$ is the potential energy operator. We can discretize this equation obtaining a finite differences approach:

$$-\frac{\hbar^2}{2m}\frac{\frac{\psi(x+\Delta x) - \psi(x)}{\Delta x} - \frac{\psi(x) - \psi(x-\Delta x)}{\Delta x}}{\Delta x} + U(x)\psi(x) = \varepsilon\psi(x)$$ #

If we do the identifications:

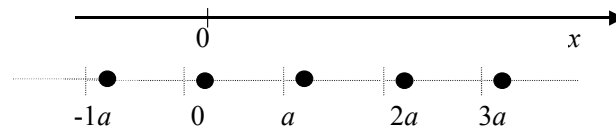$$\Delta x = a; \quad x = na; \quad L = (N+1)a$$

$$u_n = \psi(na)$$

$$E_n = U(x_n) + 2V; \quad V = -\frac{\hbar^2}{2ma^2}$$

we obtain finally:

$$(\varepsilon - E_n)u_n - Vu_{n+1} - Vu_{n-1} = 0 \quad (n = 1, 2, \ldots N)$$

Graphically this is

Therefore, we have obtained a discrete equation where the interaction is provided by the *kinetic energy* terms V which are naturally short ranged. The *local potential energy* term is given by the E_n's, and in the LCAO can be identified with the energies of atomic orbitals. What this tells us about the solution of the LCAO problem is that we can resort to the same solutions we used in the free electron problem: the plane waves. Now, instead of being written in terms of the eigenstates of the position operator $\delta(x)$ they are written in terms of the local atomic orbitals

$$|k\rangle = \sum_n u_{n,k}|n\rangle = \sum_{0 \le n < N+1} \frac{1}{\sqrt{N+1}} e^{ikna}|n\rangle$$

Let's see how it works putting these in the Schrödinger equation

$$(\varepsilon - E_0)e^{ikna} - Ve^{ik(n+1)a} - Ve^{ik(n-1)a} = 0$$

$$(\varepsilon - E_0) - Ve^{ika} - Ve^{-ika} = 0 \quad (n = 1, 2, \ldots N)$$

which is satisfied whenever

$$\varepsilon_k = E_0 + 2V\cos[ka]$$

This is the dispersion relation that defines the energy of a given wave. This relation does not provide a quantization condition yet. For that we need the **boundary conditions.**

For the **box or finite chain** condition we mix the degenerate $|k\rangle$ and $|-k\rangle$ state in a combination that satisfies

$$u_{n=0,k} = \langle n = 0|\frac{1}{\sqrt{|a|^2+|b|^2}}\{a|k\rangle + b|-k\rangle\} \equiv 0$$

which is satisfied for $a = -b = i/\sqrt{2}$

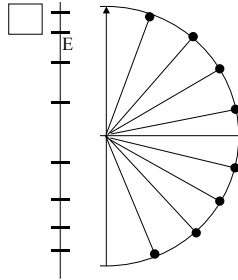$$u_{n,k} = \langle n|k \rangle = \sqrt{\tfrac{2}{N+1}}\, \sin[kna]$$

the other boundary condition would require that the wave function is zero at site $N + 1$, i.e.

$$u_{N+1,k} = \langle N+1|k \rangle = \sqrt{\tfrac{2}{N+1}}\, \sin[k(N+1)a] \equiv 0$$

now the only freedom to satisfy this condition is to select the appropriate wave number k.

$$k_m(N+1)a = m\pi \ \ \text{for}\ \ m = 1,2,3\dots N$$

i.e. we have achieved the quantization. Notice that when N is an odd number we will have $E_k = 0$ for $m = \frac{1}{2}(N+1)$.

Eigenenergies for $N = 8$ orbitals.

  Exercise. Verify that for $N = 2, 3$, and 4 this solution coincides with the one obtained directly from the secular equation.

  The **periodic or ring case**, the eigenfunctions can be complex showing that they support a finite current and the degeneracy indicates that current can either be forward or backward. The boundary condition would require that the wave function be single valued and is obtained requiring

$$u_{1,k} \equiv u_{N+1,k} \ \ \text{or}\ \ e^{\pm ika} \equiv e^{\pm ik(N+1)a}$$

$$kN = m2\pi \ \ m = 0,1,2,3,N-1.$$

Notice that the minimal energy can be achieved with the quantum number $m = 0$. We will see this is the boundary condition again that one has to use to obtain the eigenstates and molecular orbitals in a **benzene** molecule which corresponds to the case $N = 6$.

Basic Many particle Systems

Two electron atoms.

Supose the the two particle Schrödinger equation is separable. Hence solutions of the form $\varphi_n(\mathbf{r}_1)\varphi_m(\mathbf{r}_2)$ and $\varphi_m(\mathbf{r}_1)\varphi_n(\mathbf{r}_2)$ have both the same energy $E = \varepsilon_n + \varepsilon_m$.

$$\Psi_{n,m}(\mathbf{r}_1,\mathbf{r}_2) = [A\varphi_n(\mathbf{r}_1)\varphi_m(\mathbf{r}_2) + B\varphi_m(\mathbf{r}_1)\varphi_n(\mathbf{r}_2)]$$

with the condition that $|A|^2 + |B|^2 = 1$.

If we include the electron electron interaction the value of expectation of the energy

$$\langle E \rangle = \int\int \Psi_{n,m}^*(\mathbf{r}_1,\mathbf{r}_2)(H_1 + H_2 + U)\Psi_{n,m}(\mathbf{r}_1,\mathbf{r}_2)\mathrm{d}^3\mathbf{r}_1,\mathrm{d}^3\mathbf{r}_2$$

$$= \varepsilon_n + \varepsilon_m + \langle nm|U|nm\rangle - 2AB\langle nm|U|nm\rangle$$

This is a first order calculation, but we still can expect that the best wave function is that that minimizes the energy. Since the exchange intergral is definite positive, the minimal energy is obtained when $A = -B = 1/\sqrt{2}$. Hence

$$\Psi_{n,m}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}} \underbrace{[\varphi_n(\mathbf{r}_1)\varphi_m(\mathbf{r}_2) - \varphi_m(\mathbf{r}_1)\varphi_n(\mathbf{r}_2)]}_{\text{antisymmetric with exchange of space coordinates}}$$

This was analized by Heisenberg to realize that two Fermions with the same spin can not occupy the same point in space and hence the Coulomb repulsion would be greatly diminished. Notably, this occurs even when the eigenstates have different quantum numbers n and m, this is because inded position is a quantum number for the position operator the Pauli principle states that no electrons could occupy the same states (not necessarily eigenstates).

It was Slater who was able to generalize this concept to include spin. Spin has to be added in the double role as a quantum number and as a coordinate. Let's see how this works.

$$\Psi_{\alpha,\beta}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_\alpha(\mathbf{r}_1) & \psi_\alpha(\mathbf{r}_2) \\ \psi_\beta(\mathbf{r}_1) & \psi_\beta(\mathbf{r}_2) \end{vmatrix}$$

Let us assume that the spin state is equal while the orbital quantum numbers are different, i.e. the states are $\alpha = n,\uparrow$ and $\beta = m,\uparrow$.

$$\Psi_{\alpha,\beta}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_n(\mathbf{r}_1)\uparrow_1 & \varphi_n(\mathbf{r}_2)\uparrow_2 \\ \varphi_m(\mathbf{r}_1)\uparrow_1 & \varphi_m(\mathbf{r}_2)\uparrow_2 \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}}[\varphi_n(\mathbf{r}_1)\varphi_m(\mathbf{r}_2)\uparrow_2 \uparrow_1 - \varphi_m(\mathbf{r}_1)\varphi_n(\mathbf{r}_2)\uparrow_2 \uparrow_1]$$

$$= \frac{1}{\sqrt{2}} \underbrace{[\varphi_n(\mathbf{r}_1)\varphi_m(\mathbf{r}_2) - \varphi_m(\mathbf{r}_1)\varphi_n(\mathbf{r}_2)]}_{\text{antisymmetric with respect to exchange of space coord.}} \times \uparrow_2 \uparrow_1$$

i.e. the spacial part is itself a determinant.

Slater determinant and Hartree-Fock

The Hartree-Fock procedure proposes that the ground state is described by a single Slater

determinant of the form

$$\Psi_{\alpha,\beta,...N}(\mathbf{r}_1,\mathbf{r}_2,...\mathbf{r_N}) = \frac{1}{\sqrt{N}} \begin{vmatrix} \psi_\alpha(\mathbf{r}_1) & \psi_\alpha(\mathbf{r}_2) & ... & \psi_\alpha(\mathbf{r}_N) \\ \psi_\beta(\mathbf{r}_1) & \psi_\beta(\mathbf{r}_2) & ... & \psi_\beta(\mathbf{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(\mathbf{r}_1) & \psi_N(\mathbf{r}_2) & ... & \psi_N(\mathbf{r}_N) \end{vmatrix}$$

Fixed the Hilbert space for the single particle wave funtions. The Slater determinant that minimises the energy is formed by the lowest energy eigenstates $\psi_\alpha(\mathbf{r})$ of an effective Schrödinger equation. The Hartree Fock equation for a system with N electrons is an iterative procedure according to which one uses the eigenfuntion evaluated in the order (n-1) to evaluate those of the order (n). Only the lowest N occupied functions enter in the calculation of the effective potential. However, in a generalized calculation the occupation may be fractional and are determined by thermal Fermi factor $\sum_\beta f_\beta = N$. The calculation proceeds within the Hilbert space spanned by a finite basis:

$$\varepsilon_\alpha \psi_\alpha^{(s)}(\mathbf{r}) = [-\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r})]\psi_\alpha^{(s)}(\mathbf{r})$$

$$+ \underbrace{\left[\int d\mathbf{r}' \sum_\beta f_\beta \psi_\beta^{*(s-1)}(\mathbf{r}')\psi_\beta^{(s-1)}(\mathbf{r}')U(\mathbf{r}' - \mathbf{r}) \right]}_{\textit{direct potential (local)}} \psi_\alpha^{(s)}(\mathbf{r})$$

$$- \int d\mathbf{r}' \underbrace{\left[\sum_\beta f_\beta \psi_\beta^{*(s-1)}(\mathbf{r}')\psi_\beta^{(s-1)}(\mathbf{r})U(\mathbf{r}' - \mathbf{r}) \right]}_{\textit{exchange (non-local)}} \psi_\alpha^{(s)}(\mathbf{r}')$$

Notice that the last term plays a similar role as the kinetic energy term. It tries to delocalize the electron. In a discretized representation it is clear that the laplacian mixes amplitudes at different positions of the space

$$[-\frac{\hbar^2 \nabla^2}{2m}]\psi_\alpha^{(s)}(\mathbf{r}) \Rightarrow -\frac{\hbar^2}{2ma^2}\left[\psi_\alpha^{(s)}(\mathbf{r}_{n-1}) - 2\psi_\alpha^{(s)}(\mathbf{r}_n) + \psi_\alpha^{(s)}(\mathbf{r}_{n+1}) \right]$$

a similar effect is obtained from the exchange term. Now, however the exchange "hopping" has a longer range which is determined by the Coulomb interaction.

An option is to express the Hartree Fock equations in terms of a given basis. What the intergro-differential equation becomes an algebraic equation again to be solved self-consistently:

$$\hat{f}_1 \phi_n = \varepsilon_n \phi_n$$

with

$$\hat{f}_1 = \{\hat{H}_1 + \sum_{m=1}^{N} [J_m + K_m\}$$

and

$$J_m(1)\phi_n = \left\{ \int d^3\mathbf{r}_2 (\phi_m^*(\mathbf{r}_2)\phi_m(\mathbf{r}_2)) \frac{e^2}{|\mathbf{r}_2 - \mathbf{r}_1|} \right\} \phi_n(\mathbf{r}_1)$$

is a diagonal term in this orgital basis while the exchange term mixes orbitals in the basis

$$K_m(r_1)\phi_n = \left\{ \int d^3\mathbf{r}_2 (\phi_m^*(\mathbf{r}_2)\phi_n(\mathbf{r}_2)) \frac{e^2}{|\mathbf{r}_2 - \mathbf{r}_1|} \right\} \phi_m(\mathbf{r}_1)$$

in particular if we select as a basis the discrete finite elements.

Meaning of H-F eigenvalues

Let's remember that the total energy is not juste the summ of the single particle energies but it is:

$$E_{HF}(N) = \sum_{k=1}^{N} \varepsilon_k - \underbrace{\frac{1}{2} \sum_{k,l=1}^{N} [\langle kl|U|kl\rangle - \langle kl|U|lk\rangle]}_{\text{positive}}$$

$$= \frac{1}{2} \sum_{k=1}^{N} (\varepsilon_k + \langle k|T + V|k\rangle)$$

From the first equality we see that the total energy is not just the summ of single particle energies (that includes interactions) but it is something smaller. Still there is an atempt to recover the single particle description.

The Koopman's theorem says that if we evaluate the HF energy evaluated with N particles and compares it the energy calculated with the Slater determinant resulting from the removal of orbital k i.e. with N-1 particles the describes the ionization energy:

$$I_k = E_{HF}(N-1_k) - E_{HF}(N)$$

$$= -\varepsilon_k$$

Of course, this assumes that the spin-orbitals are frozen after the electron removal.

Similarly we can describe the enegy required to remove an electron from occupied state l and place it at unoccupied state k

$$\Delta_{l,k} = \varepsilon_k - \varepsilon_l - [\langle kl|U|kl\rangle - \langle kl|U|lk\rangle]$$

the term in square bracket goes to zero as the volume goes to infinity. Within the approximation stated above, this also gives a meaning to the unoccupied orbitals evaluated in a HF procedure.