1 Quantum Mechanincs In 1D

2 Quantum Erasers

3 Spherical Harmonics

3.1 Feynman's Trick

Consider the Spherical Harmonic,

$$Y_m^\ell(\theta,\phi) = \langle\theta,\phi|\ell,m\rangle$$

Now denote the state with total angular momentum $\ell(\ell+1)$ and component m along the axis defined by (θ,ϕ) as $|\ell,m,\theta,\phi\rangle$. That is,

$$|\ell,m,\theta,\phi\rangle = R(\theta,\phi)\,|\ell,m\rangle$$

These states with fixed (θ,ϕ) and ℓ varying over m form a complete set of states for the fixed ℓ-multiplet subspace. thus,

$$Y_m^\ell(\theta,\phi) = \langle\theta,\phi|\ell,m\rangle = \sum_{m'=-\ell}^{\ell} \langle\theta,\phi|\ell,m',\theta,\phi\rangle\,\langle\ell,m',\theta,\phi|\ell,m\rangle$$

However, it is easily shown that,

$$\langle\theta,\phi|\ell,m',\theta,\phi\rangle = \langle+z|\,R(\theta,\phi)^\dagger R(\theta,\phi)\,|\ell,m'\rangle = \langle+z|\ell,m'\rangle = Y_{m'}^\ell(0,0)$$

is zero unless $m=0$. Thus we find,

$$Y_m^\ell(\theta,\phi) = Y_0^\ell(0,0)\,\langle\ell,0,\theta,\phi|\ell,m\rangle = Y_0^\ell(0,0)\,\langle\ell,0|\,R(\theta,\phi)^\dagger\,|\ell,m\rangle$$

which agrees with Feynman's formula.

4 Multi-Electron Atoms

4.1 The Born-Oppenheimer Approximation

4.2 Exchange Energies

First consider two electrons in a central nuclear potential with Hamiltonian,

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \frac{e^2}{|r_1 - r_2|} = \frac{\hat{p}_1^2}{2m_e} + \frac{\hat{p}_2^2}{2m_e} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|r_1 - r_2|}$$

where $\hat{H}_1 = \hat{H}_e \otimes I_2$ and $\hat{H}_2 = I_1 \otimes \hat{H}_e$ and,

$$\hat{H}_e = \frac{\hat{p}^2}{2m_e} - \frac{Ze^2}{r}$$

Consider two electrons in states $|\psi\rangle$ and $|\phi\rangle$ given by the slater determinant,

$$|\Psi\rangle = \frac{1}{\sqrt{2}}\left[|\psi\rangle \otimes |\phi\rangle - |\phi\rangle \otimes |\psi\rangle\right]$$

Note we may require $\langle\psi|\psi\rangle = \langle\phi|\phi\rangle = 1$ and $\langle\psi|\phi\rangle = 0$ without loss of generality since any parallel term is removed in the antisymmetrization. Now consider,

$$\begin{aligned}
\langle\Psi|\,\hat{H}\,|\Psi\rangle = \frac{1}{2}&\left[\langle\psi|\,\hat{H}_e\,|\psi\rangle + \langle\phi|\,\hat{H}_e\,|\phi\rangle + \langle\psi|\otimes\langle\phi|\,\frac{e^2}{|r_1-r_2|}\,|\psi\rangle\otimes|\phi\rangle\right]\\
-\frac{1}{2}&\left[\langle\psi|\,\hat{H}_e\,|\phi\rangle\,\langle\phi|\psi\rangle + \langle\psi|\phi\rangle\,\langle\phi|\,\hat{H}_e\,|\psi\rangle + \langle\psi|\otimes\langle\phi|\,\frac{e^2}{|r_1-r_2|}\,|\phi\rangle\otimes|\psi\rangle\right]\\
-\frac{1}{2}&\left[\langle\phi|\,\hat{H}_e\,|\psi\rangle\,\langle\psi|\phi\rangle + \langle\phi|\psi\rangle\,\langle\psi|\,\hat{H}_e\,|\phi\rangle + \langle\phi|\otimes\langle\psi|\,\frac{e^2}{|r_1-r_2|}\,|\psi\rangle\otimes|\phi\rangle\right]\\
+\frac{1}{2}&\left[\langle\phi|\,\hat{H}_e\,|\phi\rangle + \langle\psi|\,\hat{H}_e\,|\psi\rangle + \langle\phi|\otimes\langle\psi|\,\frac{e^2}{|r_1-r_2|}\,|\phi\rangle\otimes|\psi\rangle\right]
\end{aligned}$$

We may combine these matrix ellements to find,

$$\begin{aligned}
\langle\Psi|\,\hat{H}\,|\Psi\rangle = &\langle\psi|\,\hat{H}_e\,|\psi\rangle + \langle\phi|\,\hat{H}_e\,|\phi\rangle + \langle\psi|\otimes\langle\phi|\,\frac{e^2}{|r_1-r_2|}\,|\psi\rangle\otimes|\phi\rangle\\
&-\langle\phi|\otimes\langle\phi|\,\frac{e^2}{|r_1-r_2|}\,|\phi\rangle\otimes|\phi\rangle
\end{aligned}$$

This is the energy we expect for the first electron in state $|\psi\rangle$ and the second in state $|\phi\rangle$ except for the last term, the exchange energy,

$$\begin{aligned}
E_{\text{ex}} = -\langle\phi|\otimes\langle\phi|\,\frac{e^2}{|r_1-r_2|}\,|\phi\rangle\otimes|\phi\rangle = -\int \mathrm{d}^3x\,\mathrm{d}^3y\,\phi^*(x)\psi^*(y)\frac{e^2}{|\vec{x}-\vec{y}|}\psi(x)\phi(y)\\
-\int \mathrm{d}^3x\,\mathrm{d}^3y\,\frac{e^2}{|\vec{x}-\vec{y}|}\psi(x)\phi^*(x)\psi^*(y)\phi(y)
\end{aligned}$$

4.3 Hartee-Fock Theory

The wavefunction of an arbitrary n-electron state must be totally antisymmetric. Given an orthonormal set of n single-electron states the closest mult-electron state which satisfies the proper fermionic condition is given by a Slater determinant,

$$\Psi(x_1,\cdots,x_n) = \frac{1}{\sqrt{n!}}\begin{vmatrix}\psi_1(x_1) & \psi_1(x_2) & \cdots & \psi_1(x_n)\\ \psi_2(x_1) & \psi_2(x_2) & \cdots & \psi_2(x_n)\\ \vdots & \vdots & \ddots & \vdots\\ \psi_n(x_1) & \psi_n(x_2) & \cdots & \psi_n(x_n)\end{vmatrix}$$

Where ψ_i is the i-th spin-orbital i.e. the variable x_i lives in the product space of position and spin degrees of freedom. Explicity, $x = (\vec{r}, s)$ and $\psi_i(x) = (\langle\vec{r}|\otimes\langle s|)\,|\psi_i\rangle$. Recall that this multi-electron state is only properly normalized if we require that,

$$\langle\psi_i|\psi_j\rangle = \delta_{ij}$$

Our first task is to compute the energy of such a Slater determinant. Recall that, under the Born-Oppenhiemer approximation, the multi-electron Hamiltonian is,

$$\hat{H} = \sum_{i=1}^{n} \left[\frac{\vec{p}_i^{\,2}}{2m_e} - \sum_{j=1}^{N} \frac{Z_j e^2}{|\vec{r}_i - \vec{R}_j|} \right] + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} = \sum_{i=1}^{n} \hat{H}_S^{(i)} + \frac{1}{2} \sum_{i \neq j} \hat{H}_R^{(ij)}$$

where $\hat{H}_S$, the single particle Hamiltonian acts on the product space as a product, and $\hat{H}_R$ only mixes pairs of spaces. Thus we have,

$$\begin{aligned} E_\Psi &= \langle \Psi | \hat{H} | \Psi \rangle = \sum_{i=1}^{n} \langle \Psi | \hat{H}_S^{(i)} | \Psi \rangle + \frac{1}{2} \sum_{i \neq j} \langle \Psi | \hat{H}_R^{(ij)} | \Psi \rangle \\ &= \frac{1}{n!} \sum_{\sigma,\tau \in S_n} \sum_{i=1}^{n} (-1)^{\text{sign}(\sigma)+\text{sign}(\tau)} \left\langle \psi_{\sigma(1)} \right| \otimes \cdots \otimes \left\langle \psi_{\sigma(n)} \right| \hat{H}_S^{(i)} \left| \psi_{\tau(1)} \right\rangle \otimes \cdots \otimes \left| \psi_{\tau(n)} \right\rangle \\ &+ \frac{1}{2n!} \sum_{\sigma,\tau \in S_n} \sum_{i \neq j} (-1)^{\text{sign}(\sigma)+\text{sign}(\tau)} \left\langle \psi_{\sigma(1)} \right| \otimes \cdots \otimes \left\langle \psi_{\sigma(n)} \right| \hat{H}_R^{(ij)} \left| \psi_{\tau(1)} \right\rangle \otimes \cdots \otimes \left| \psi_{\tau(n)} \right\rangle \end{aligned}$$

Now if $\sigma \neq \tau$ then there are at least two values which differ between them (since σ and τ are permuations). Therefore, the first inner product is zero unless $\sigma = \tau$. Thus, the single particle Hamiltonian gives a contribution,

$$\frac{1}{n!} \sum_{\sigma \in S_n} \sum_{i=1}^{n} \left\langle \psi_{\sigma(1)} \right| \otimes \cdots \otimes \left\langle \psi_{\sigma(n)} \right| \hat{H}_S^{(i)} \left| \psi_{\sigma(1)} \right\rangle \otimes \cdots \otimes \left| \psi_{\sigma(n)} \right\rangle = \frac{1}{n!} \sum_{\sigma \in S_n} \sum_{i=1}^{n} h_{\sigma(i)} = \sum_{i=1}^{n} h_i$$

where

$$h_i = \langle \psi_i | \hat{H}_S | \psi_i \rangle$$

since the sum over such values is invariant under permutation. Now consider the two-electron repulsion terms,

$$\frac{1}{n!} \sum_{\sigma,\tau \in S_n} \sum_{i \neq j} (-1)^{\text{sign}(\sigma)+\text{sign}(\tau)} \left\langle \psi_{\sigma(1)} \right| \otimes \cdots \otimes \left\langle \psi_{\sigma(n)} \right| \hat{H}_R^{(ij)} \left| \psi_{\tau(1)} \right\rangle \otimes \cdots \otimes \left| \psi_{\tau(n)} \right\rangle$$

Since all but two of the single-particle states must correspond for the inner product to be nonzero, the only non-equal option is that σ and τ differ by a single transposition, that is, $\sigma = \tau \circ (a\ b)$. Thus, the repulsion terms become,

$$\begin{aligned} &\frac{1}{n!} \sum_{\sigma \in S_n} \sum_{i \neq j} \left\langle \psi_{\sigma(1)} \right| \otimes \cdots \otimes \left\langle \psi_{\sigma(n)} \right| \hat{H}_R^{(ij)} \left| \psi_{\sigma(1)} \right\rangle \otimes \cdots \otimes \left| \psi_{\sigma(n)} \right\rangle \\ &- \frac{1}{n!} \sum_{\sigma \in S_n} \sum_{a<b} \sum_{i \neq j} \left\langle \psi_{\sigma(1)} \right| \otimes \cdots \otimes \left\langle \psi_{\sigma(n)} \right| \hat{H}_R^{(ij)} \left| \psi_{\sigma(1)} \right\rangle \otimes \cdots \otimes \left| \psi_{\sigma(n)} \right\rangle \\ &\frac{1}{n!} \sum_{\sigma \in S_n} \sum_{i \neq j} J_{\sigma(i)\sigma(j)} - \frac{1}{n!} \sum_{\sigma \in S_n} \sum_{i \neq j} K_{\sigma(i)\sigma(j)} \\ &= \sum_{i \neq j} [J_{ij} - K_{ij}] \end{aligned}$$

where,

$$J_{ij} = \langle\psi_i| \otimes \langle\psi_j| H_R |\psi_i\rangle \otimes |\psi_j\rangle = \int \mathrm{d}^3x_1\, \mathrm{d}^3x_2\, \psi_i^*(x_1)\psi_j^*(x_2)\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}\psi_i(x_1)\psi_j(x_2)$$
$$K_{ij} = \langle\psi_i| \otimes \langle\psi_j| H_R |\psi_j\rangle \otimes |\psi_i\rangle = \int \mathrm{d}^3x_1\, \mathrm{d}^3x_2\, \psi_i^*(x_1)\psi_j^*(x_2)\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}\psi_j(x_1)\psi_i(x_2)$$

Note that if $|\psi_i\rangle$ and $|\psi_j\rangle$ are product states in the spin degrees of freedom then K_{ij} is zero for opposite spin states. Thus, finally, the energy becomes,

$$E_\Psi = \langle\Psi| \hat{H} |\Psi\rangle = \sum_{i=1}^{n} h_i + \frac{1}{2}\sum_{i,j=1}^{n}[J_{ij} - K_{ij}]$$

Note that we may include the $i = j$ cross terms noting that $K_{ii} = J_{ii}$. Now we use the variational principal with respect to the states $|\psi_1\rangle$ subject to the constraint,

$$\langle\psi_1|\psi_j\rangle = \delta_{ij}$$

Therefore we introduce Largange multipliers and set the variation to zero,

$$\frac{\delta}{\delta\psi_i^*(x)}\left[\langle\Psi| \hat{H} |\Psi\rangle - \sum_{i,j=1}^{n}(\langle\psi_i|\psi_j\rangle - \delta_{ij})\varepsilon_{ij}\right] = 0$$

Therefore,

$$\left(\hat{H}_S + \sum_{j=1}^{n}[\hat{J}_j - \hat{K}_j]\right)\psi_i(x) = \sum_{j=1}^{n}\varepsilon_{ij}\psi_j(x)$$

where,

$$\hat{J}_j\psi(x) = \left[\int \mathrm{d}^3x_j\, \psi_j^*(x_j)\frac{e^2}{|\vec{r} - \vec{r}_j|}\psi_j(x_j)\right]\psi(x)$$
$$\hat{K}_j\psi(x) = \left[\int \mathrm{d}^3x_j\, \psi_j^*(x_j)\frac{e^2}{|\vec{r} - \vec{r}_j|}\psi(x_j)\right]\psi_j(x)$$

Thus we have derived the Fock operator,

$$\hat{F} = \hat{H}_S + \sum_{j=1}^{n}[\hat{J}_j - \hat{K}_j]$$

It remains to solve this pseudo-eigenvalue problem with the nonlinear operators. First, let U_{ij} be an $n \times n$ special unitary matrix. Consider the transformation,

$$|\psi_i'\rangle = \sum_{j=1}^{n} U_{ij}\,|\psi_j\rangle$$

which preserves the inner product,

$$\langle \psi_i' | \psi_j' \rangle = \sum_{k,\ell=1}^{n} \langle \psi_k | \psi_\ell \rangle \, U_{ik}^* U_{j\ell} = \sum_{k,\ell=1}^{n} \delta_{k\ell} U_{ik}^* U_{j\ell} = \sum_{k=1}^{n} \langle \psi_k | \psi_\ell \rangle \, U_{jk} (U^\dagger)_{ki} = \delta_{ij}$$

Now consider the matrix,

$$\begin{pmatrix} \psi_1'(x_1) & \psi_1'(x_2) & \cdots & \psi_1'(x_n) \\ \psi_2'(x_1) & \psi_2'(x_2) & \cdots & \psi_2'(x_n) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_n'(x_1) & \psi_n'(x_2) & \cdots & \psi_n'(x_n) \end{pmatrix} = \begin{pmatrix} U_{11} & U_{12} & \cdots & U_{1n} \\ U_{21} & U_{22} & \cdots & U_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ U_{n1} & U_{n2} & \cdots & U_{nn} \end{pmatrix} \begin{pmatrix} \psi_1(x_1) & \psi_1(x_2) & \cdots & \psi_1(x_n) \\ \psi_2(x_1) & \psi_2(x_2) & \cdots & \psi_2(x_n) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_n(x_1) & \psi_n(x_2) & \cdots & \psi_n(x_n) \end{pmatrix}$$

Since $\det U = 1$ thus we have shown that the determinant of this matrix remains unchanged and thus $|\Psi'\rangle = |\Psi\rangle$. Therefore, transforming a solution set of single-electron wave functions via U will not change of the physical wavefunction and thus still represent an energy minimum. Since ε_{ij} is a symmetric matrix, it can be diagonalized via a special unitary matrix U. Therefore, we can apply such a transformation to make the representing single-electron wavefunction eigenvectors of the matrix ϵ_{ij} to reduce the Fock equation to the eigenvalue form,

$$\hat{F}\psi_i = \varepsilon_i \psi_i$$

5 Time Independent Perturbation Theory

5.1 Non-Degenerate Perturbation Theory

5.2 First-Order

5.2.1 Second-Order Non-Degenerate Perturbation Theory

5.2.2 Higher-Order Non-Degenerate Perturbation Theory

6 Degenerate Perturbation Theory

6.1 First-Order Degenerate Perturbation Theory

6.1.1 Second-Order Degenerate Perturbation Theory

7 Symmetries and Conservation

8 Wigner's Theorem

8.1 Quantum Dynamics

8.1.1 Unitary Time Evolution

8.1.2 The Heisenberg Picture

8.1.3 The Interaction Picture

8.2 The Adjoint Representation

(DEGENERACY) (WINGER THEOREM)

9 Representation Theory

9.1 Tensor Operators

9.2 The Wigner-Eckart Theorem

10 Angular Momentum

11 The Radial Equation

12 The Harmonic Oscillator

12.1 The Explicit Series Solution

12.2 The Operator Method

12.3 Coherent States

12.4 Squeezed States

12.5 Multidimensional Harmoic Oscilators

(SYMMETRY SU(N))

12.6 Coupled Oscillators

13 The Hydrogen Atom

13.1 The Non-Relativistic Solution

13.1.1 The Explicit Series Solution

13.1.2 The Operator Method

13.2 Hidden Symmetry of the Coulomb Problem

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