Chapter 8

Variational Principle

8.1 General Idea:

Consider a physical system described by a Hamiltonian $\hat{H}$. Let's write H in terms of its eigen-decomposition $H = \sum_i E_i|\phi_i\rangle\langle\phi_i|$ where we suppose that the energy levels are labelled in increasing order with $E_i \leq E_{i+1}$ with E_0 the ground state energy. It follows that for any state $|\psi\rangle$, the average energy of that state $\langle\psi|H|\psi\rangle$, will always be greater than or equal to the ground state energy E_0. This rather obvious[1] statement is given the name of the *variational principle*:

$$\langle\psi|H|\psi\rangle \geq E_0 .$$

This inequality becomes an quality (again obviously) if and only if $|\psi\rangle = |\phi_0\rangle$, and ϕ_0 is non-degenerate. I think this statement hardly needs proving but in case its helpful here is that proof in the discrete case (and the continuous case easily follows by using properties of the integral):

$$\begin{aligned}
\langle\psi|\hat{H}|\psi\rangle &= \sum_{n=0}^{\infty} E_n \left|\langle\psi|\phi_n\rangle\right|^2 \\
&\geq E_0 \sum_{n=0}^{\infty} \left|\langle\psi|\phi_n\rangle\right|^2 \\
&= E_0 \sum_{n=0}^{\infty} \langle\psi|\phi_n\rangle\langle\phi_n|\psi\rangle \\
&= E_0
\end{aligned}$$

Note that I have provided the statement above assuming, as is standard, that the state $|\psi\rangle$ is normalised. However, the variational principle is often stated more generally for the case of a (potentially) non-normalized state. In this case you first need to normalize by hand such that $|\psi\rangle$ becomes $\frac{1}{\sqrt{\langle\psi|\psi\rangle}}|\psi\rangle$ and so the variational principle becomes:

$$\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0 . \tag{8.1}$$

We can use the variational principle to find an approximation of the ground state of H. The idea is to come up with a parameterised guess for the state $|\psi\rangle$, and then we use the variational

[1] I generally try and avoid calling things 'trivial' or 'obvious' but I really do think this statement is. And recognising so is actually helpful. Of course the lowest energy a state can have is the ground state energy! As a result I've always found naming this claim as the 'variational principle' at best a bit grandiose and at worst slightly confusing.

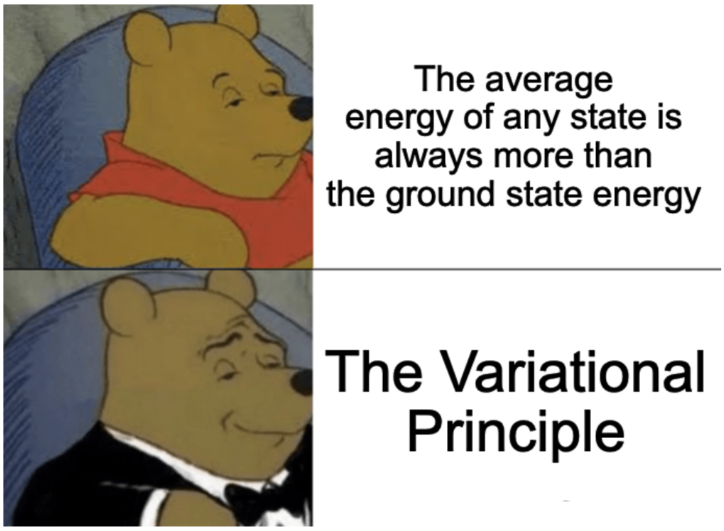

Figure 8.1:

principle to find the parameter values that minimize ψ. This method generalizes to excited states. For any $|\psi\rangle \in \mathcal{H}$ such that $\langle\phi_0|\psi\rangle = 0$, the following inequality[2] is always satisfied:

$$\frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_1.$$

The proof of this fact is identical to the proof of the variational principle for the ground state since the term involving $|\phi_0\rangle$ drops out by the choice of $|\psi\rangle$.

Ok, so the basic idea of the variational principle is pretty simple (I promise!). Let's now look at how it is applied in practise. Again, I hope you'll agree that the basic idea of how to apply it is straightforward enough. That said, as we'll see, actually doing the full calculation can lead to some annoying integrals.

Example 8.1.1 (One-Dimensional Harmonic Oscillator). The system's Hamiltonian is given by:

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}}_{=\hat{T}} + \underbrace{\frac{1}{2}m\omega^2 x^2}_{=\hat{V}}. \tag{8.2}$$

We introduce a (non-normalized) trial function:

$$\psi_a(x) = \frac{1}{x^2 + a} \tag{8.3}$$

with $a > 0$. Note that this choice is physically unrealistic because the wavefunction should decrease exponentially as x goes to infinity. Our goal is to compute the energy of H in the state

[2] We're assuming here that the ground state is non-degenerate. If it's degenerate you need the constraint that $|\psi\rangle$ has zero overlap onto the space spanned by the ground states.

$|\psi\rangle$ and then find the a that minimizes this energy. To do so, we need to compute:

$$\begin{aligned}\langle\psi|\hat{T}|\psi\rangle &= -\frac{\hbar^2}{2m}\int_{-\infty}^{\infty} dx \frac{1}{x^2+a}\frac{d^2}{dx^2}\frac{1}{x^2+a} \\ \langle\psi|\hat{V}|\psi\rangle &= \frac{1}{2}m\omega^2\int_{-\infty}^{\infty} dx \frac{x^2}{(x^2+a)^2} \\ \langle\psi|\psi\rangle &= \int_{-\infty}^{\infty} dx \frac{1}{(x^2+a)^2}\,.\end{aligned} \tag{8.4}$$

This will allow us to compute the average energy of our guess as a function of x as

$$E(x) := \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\langle\psi|\hat{T}|\psi\rangle}{\langle\psi|\psi\rangle} + \frac{\langle\psi|\hat{V}|\psi\rangle}{\langle\psi|\psi\rangle}\,. \tag{8.5}$$

And then all we need to do is find the minimum of the function $E(x)$, and this will be our guess of the ground state energy.

Computing the integrals is the hard part. I'll leave that fun to you and just state the results here [3].

$$\langle\psi|\psi\rangle = \int_{-\infty}^{\infty} \frac{1}{(x^2+a)^2}dx = \frac{\pi}{2a^{3/2}} \tag{8.6}$$

$$\begin{aligned}\langle\psi|\hat{H}|\psi\rangle &= \int_{-\infty}^{\infty} \frac{1}{x^2+a}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2\right)\frac{1}{x^2+a}dx \\ &= -\frac{\hbar^2}{2m}\int_{-\infty}^{\infty} \frac{6x^2-2a}{(x^2+a)^4}dx + \frac{1}{2}m\omega^2\int_{-\infty}^{\infty} \frac{x^2}{(x^2+a)^2}dx \\ &= \frac{\pi}{2a^{3/2}}\left(\frac{\hbar^2}{4ma} + \frac{1}{2}m\omega^2 a\right)\,.\end{aligned} \tag{8.7}$$

The energy corresponding to a state $|\psi_a\rangle$ is therefore given by

$$E(a) = \frac{\langle\psi_a|\hat{H}|\psi_a\rangle}{\langle\psi_a|\psi_a\rangle} = \frac{\hbar^2}{4m}\frac{1}{a} + \frac{1}{2}m\omega^2 a,$$

and we seek a such that the energy is minimal:

$$\frac{dE(a)}{da} = -\frac{\hbar^2}{4ma^2} + \frac{1}{2}m\omega^2 = 0 \implies \frac{1}{2}m\omega^2a^2 = \frac{\hbar^2}{4m} \implies a = \frac{\hbar}{m\omega\sqrt{2}}.$$

Our approximation of the energy of the ground state is therefore given by

$$E\left(\frac{\hbar}{m\omega\sqrt{2}}\right) = \frac{\hbar\omega}{\sqrt{2}} \simeq 0.72\hbar\omega \tag{8.8}$$

This approximation is considerably higher than the exact (known in the case of the harmonic oscillator) ground state energy: $0.72\hbar\omega > 0.5\hbar\omega$.

[3] Don't worry, in the exam I'll give you enough hints for you to be able to figure it out without being an integration wizard. If you want some hints for this one, go check out Vincenzo's notes.

Example 8.1.2 (One-Dimensional Harmonic Oscillator:). We could now similarly determine the first excited state of the one-dimensional harmonic oscillator. The Hamiltonian is still given by Eq. 8.2. Let's set [4] $\psi_a(x))\frac{x}{(x^2+a)^2}$ with $a > 0$. This function is odd under the inversion $x \to -x$. Therefore, it will be orthogonal to the ground state $\psi_0(x)$, which is even.

For the computation, we will need the following integrals:

$$I_4 = \int_{-\infty}^{\infty} dx \frac{1}{(x^2+a)^4} = \frac{5\pi}{16} a^{-7/2} \qquad I_5 = \frac{35\pi}{128} a^{-9/2}$$

$$J_4 = \int_{-\infty}^{\infty} \frac{x^2}{(x^2+a)^4} = \frac{\pi}{16} a^{-5/2} \qquad I_6 = \frac{63\pi}{256} a^{-11/2}$$

$$k_4 = \int_{-\infty}^{\infty} dx \frac{x^4}{(x^2+a)^4} = \frac{\pi}{16} a^{-3/2}$$

It follows that we can compute the kinetic energy term as:

$$\begin{aligned}
\langle \phi_a | \hat{T} | \phi_a \rangle &= -\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} dx \frac{x^2}{(x^2+a)^2} \frac{d^2}{dx^2} \frac{x^2}{(x^2+a)^2} = \cdots \\
&= \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} dx \left(\frac{d}{dx} \frac{x}{(x^2+a)^2} \right)^2 \\
&= \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} dx \left(-\frac{1}{(x^2+a)^2} - \frac{4x^2}{(x^2+a)^3} \right)^2 \\
&= \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} dx \left(-\frac{3}{(x^2+a)^2} + \frac{4a}{(x^2+a)^3} \right)^2 \\
&= \frac{\hbar^2}{2m} \left(9I_4 - 24aI_5 + 16a^2 I_6 \right) \\
&= \frac{\hbar^2}{2m} \left(\frac{45\pi}{16} - \frac{105\pi}{16} + \frac{63\pi}{16} \right) a^{-7/2} \\
&= \frac{3}{16} \pi \frac{\hbar^2}{2m} a^{-7/2}
\end{aligned}$$

And the potential energy term is given by:

$$\begin{aligned}
\langle \phi_a | \hat{V} | \phi_a \rangle &= \frac{1}{2} m\omega^2 \int_{-\infty}^{\infty} dx \frac{x^4}{(x^2+a)^4} \\
&= \frac{1}{2} m\omega^2 k_4 \\
&= \frac{\pi}{32} m\omega^2 a^{-3/2}
\end{aligned}$$

Finally, the norm is given by:

$$\langle \phi_a | \phi_a \rangle = \int_{-\infty}^{\infty} dx \frac{x^2}{(x^2+a)^2} = J_4 = \frac{\pi}{16} a^{-5/2}$$

[4]Note we chose to divide by $(x^2+a)^2$ rather than (x^2+a^2). This is because if we picked $x/(x^2+a^2)$ then even those the function is square-integrable the potential term would eventually diverge.

Thus putting this mess together we have

$$E(a) = \frac{1}{2}\left(\frac{3\hbar^2}{m}a^{-7/2} + m\omega^2 a^{-3/2}\right) \cdot \left(a^{-5/2}\right)^{-1} = 3\frac{\hbar^2}{2m}\frac{1}{a} + \frac{1}{2}m\omega^2 a \tag{8.9}$$

To find our approximation of the energy of the first excited state we just minimize this:

$$\begin{aligned}
\frac{dE(a)}{da} &= -3\frac{\hbar^2}{2m}\frac{1}{a^2} + \frac{1}{2}m\omega^2 \\
\frac{dE(a)}{da} &\Longrightarrow \frac{3\hbar^2}{2m}\frac{1}{a^2} = \frac{1}{2}m\omega^2 \\
\Rightarrow a^2 &= \frac{3\hbar^2}{m^2\omega^2} \\
a = &= \sqrt{3}\frac{\hbar}{m\omega} \\
E_1(a) &= \frac{3\hbar^2}{2m}\frac{m\omega}{\hbar\sqrt{3}} + \frac{\sqrt{3}}{2}\hbar\omega
\end{aligned} \tag{8.10}$$

Thus we approximate the energy of the first excited state as:

$$E_1(a) = \sqrt{3}\hbar\omega \simeq 1.732\hbar\omega,$$

which is larger than, but not too far off, the known of the energy of the first excited state of the oscillator of $E_1^{\text{eff}} = 1.5\hbar\omega$.

More generally, if one cannot use a symmetry argument, one can always seek a state $|\phi\rangle$ that minimizes the energy expectation value, $E = \langle\phi|\hat{H}|\phi\rangle / \langle\phi|\phi\rangle$ with the constraint $\langle\phi|\psi\rangle = 0$, where $|\psi\rangle$ is the variational solution found for the ground state. If $|\psi\rangle$ is a good approximation, then its component orthogonal to $|0\rangle$ will be minimal. In this case, there is a high probability that the variational solution $|\phi\rangle$ will be almost orthogonal to $|0\rangle$ and will also provide a relatively good approximation to $|1\rangle$.

Note 8.1.3. Note that the variational approach makes error calculations extremely complicated (we can't do it unless we have a better approximation - but then we would just use that in the first place!) Furthermore, for any arbitrary wave function ψ, minimizing the error actually leads to restoring the Schrödinger equation.

8.2 The variational Principle for an arbitrary ansatz

These final two sections are non-examinable. I include them in case you are interested.

We can try to find the exact solution to the problem using the variational approach. Consider a Hamiltonian $\hat{H}$ and an arbitrary state $\psi(x)$. The energy expectation value is given by

$$E[\psi, \psi^*] = \langle\psi|\hat{H}|\psi\rangle = \int dx\psi^* \hat{H}\psi$$

Since ψ is a complex-valued function, we consider E to be a function of ψ and ψ^* (i.e., of $\mathfrak{R}(\psi)$ and $\mathfrak{I}(\psi)$).

Introduce an infinitesimal variation $\delta\psi^*(x)$ of $\psi^*(x)$, with $\delta\psi^*(x) \to 0$. We are treating ψ and ψ^* as two independent variables, and thus

$$E[\psi, \psi^* + \delta\psi^*] = \int dx\psi^* \hat{H}\psi + \int dx\delta\psi^* \hat{H}\psi$$

and

$$\delta E = E[\psi, \psi^* + \delta\psi^*] - E[\psi, \psi^*] = \int dx\delta\psi^* \hat{H}\psi$$

It is necessary to introduce the concept of a functional derivative at this point. Alternatively, we can imagine a function ψ "discretized" on a grid x_j, $j = -\infty, \cdots, 1, 2, \cdots$. In this case, we can interpret this problem in a variational context with an infinite number of parameters $\delta\psi_j^* = \delta^*(x_j)$. This way, we recover the concept of a traditional derivative.

To minimize E, we need $\delta E = 0$. Now,

$$\delta E = \int dx\delta\psi^* \hat{H}\psi$$

In the discretized version,

$$\delta E = \sum_j \delta\psi_j^* \hat{H}\psi_j$$

and the (true) derivative of E with respect to ψ_j^* is

$$\frac{\partial E}{\partial\psi_j^*} = \hat{H}\psi_j$$

The minimization condition is then

$$\frac{\partial E}{\partial\psi_j^*} = \ \forall j \Rightarrow \hat{H}\psi_j = 0 \ \forall j \Rightarrow \psi_j = 0$$

and similarly for ψ_j^*.

This strange result is because we forgot the norm constraint. We need $\langle\psi|\psi\rangle = 1$. And if we do not have this, we can ways just set $\psi_j = 0$ to set the energy to 0.

To find a constrained minimum, we use the Lagrange multipliers. We want to minimize $\langle\psi|\hat{H}|\psi\rangle$ with the constraint $\langle\psi|\psi\rangle = 1$. We introduce the functional

$$E[\psi, \psi^*, \lambda] = \langle\psi|H|\psi\rangle - \lambda(\langle\psi|\psi\rangle - 1) = \int dx\psi^* \hat{H}\psi - \lambda\left(\int dx\psi^*\psi - 1\right)$$

As before:

$$\delta E = \int dx \delta\psi^* \hat{H}\psi - \lambda \int dx \delta\psi^* \psi$$

The condition $\delta E = 0$ for arbitrary variation $\delta\psi^*(x)$ implies equality of the integrands:

$$\hat{H}\psi = \lambda\psi$$

It's the Schrödinger equatioN! The variational principle, without additional conditions, should lead to the exact solution of the problem (but hasn't made the problem any easier).

Reminder 8.2.1. (Harmonic Oscillator[5]). We have

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$$

with $[\hat{x}, \hat{p}] = i\hbar$. Let's introduce

$$\hat{a} \equiv \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + i\frac{1}{\sqrt{2m\hbar\omega}}\hat{p}$$
$$\hat{a}^\dagger \equiv \sqrt{\frac{m\omega}{2\hbar}}\hat{x} - i\frac{1}{\sqrt{2m\hbar\omega}}\hat{p}$$
$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}^\dagger + \hat{a})$$
$$\hat{p} = i\sqrt{\frac{m\hbar\omega}{2}}(\hat{a}^\dagger - \hat{a})$$

We note

$$[\hat{a}, \hat{a}^\dagger] = \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a} = 1$$

There is a ground state $|\phi_0\rangle$ such that

$$\hat{a}|\phi_0\rangle = 0$$

The spectrum is

$$\hat{H}|\phi_n\rangle = \hbar\omega\left(n + \frac{1}{2}\right)|\phi_n\rangle$$

The norms are

$$\hat{a}^\dagger|\phi_n\rangle = \sqrt{n+1}\,|\phi_{n+1}\rangle$$
$$\hat{a}|\phi_n\rangle = \sqrt{n}\,|\phi_{n-1}\rangle$$
$$|\phi_n\rangle = \frac{(\hat{a}^\dagger)^n}{\sqrt{N!}}|\phi_0\rangle$$

The $\{|\phi_n\rangle\}$ are non-degenerate, we thus have $\langle\phi_i|\phi_j\rangle = \delta_{ij}$.

Note 8.2.2.

$$\langle\phi_n|\hat{x}|\phi_n\rangle = \langle\phi_n|\hat{\rho}|\phi_n\rangle = 0$$

[5]Vincenzo Savona's notes, which I am working from here, have a couple of pages recapping the quantum harmonic osccilator at this point. It's not entirely clear to me why. So I will skip in the lecture. But Physicists love modelling things as a harmonic osccilator so it is good to have this stuff dialled so I'll this here in the notes in case it is helpful for anyone.

and

$$\begin{aligned}\langle\phi_n|\hat{x}^2|\phi_n\rangle &= \cdots = \frac{\hbar}{2m\omega}(2n+1)\\ \langle\phi_n|\hat{p}^2|\phi_n\rangle &= \cdots = \frac{m\hbar\omega}{2}(2n+1)\end{aligned}$$

for $n = 0$ we have $\Delta\hat{x}\Delta\hat{p} = \dfrac{\hbar}{2}$

For a Harmonic oscillator in isotropic 3D, we have

$$\hat{H} = \frac{|\hat{\mathbf{p}}|^2}{2m} + \frac{1}{2}m\omega^2|\hat{\mathbf{r}}|^2$$

Note 8.2.3.

$$\begin{aligned}|\hat{\mathbf{p}}|^2 &= \hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2\\ |\hat{\mathbf{x}}|^2 &= \hat{x}^2 + \hat{y}^2 + \hat{z}^2\end{aligned}$$

thus

$$\begin{aligned}\hat{H} &= \hat{H}_x + \hat{H}_y + \hat{H}_z\\ \hat{H} &= \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2\\ \hat{H} &= \frac{\hat{p}_y^2}{2m} + \frac{1}{2}m\omega^2\hat{y}^2\\ \hat{H} &= \frac{\hat{p}_z^2}{2m} + \frac{1}{2}m\omega^2\hat{z}^2\end{aligned}$$

Separable hamiltonian:

$$\psi(x,y,z) = \psi_n(x)\phi_m(y)\xi_l(z)$$

where $\hat{H}_x\psi_n(x) = E_n\psi(x)$, with $E_n = \hbar\omega\left(n + \dfrac{1}{2}\right)$, similarly for $\hat{y}$ and $\hat{z}$. Thus $\hat{H}\psi = E_{nml}\psi$, with $E_{nml} = \hbar\omega\left(n + m + l + \dfrac{3}{2}\right)$ Why is the harmonic oscillator so important?

1. Except for pathological cases, all systems admit a harmonic approximation.

   Example 8.2.4. Central Potential. We have

   $$V = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + \frac{L^2}{2mr^2} - \frac{\alpha}{r}$$

   One could start from the solution of the harmonic problem and calculate more accurate solutions using perturbation theory.

2. Quantum Field Theory for Multi-Body Systems. The state of a free particle with momentum $\hbar k$ corresponding to one quantum of energy can be written as $|1\rangle$. Thus, two particles in the same state will have twice the energy, which can be understood as the state $|2\rangle$ of the harmonic oscillator, and so on. The states of N free particles are described as an infinite set of harmonic oscillators, one for each $\hbar\mathbf{k}$.

More formally, this result can be obtained from the consideration that the wave function $\psi(\mathbf{r})$ can be treated as a dynamic variable, and thus as an additional operator, denoted by $\hat{\psi}$ and $\hat{\psi}^\dagger$. This procedure is called second quantization.

8.3 Hartree-Fock Theory

Let's consider a system of N spinless Fermions. If you've forgotten the lecture of indistinguishable particles now might be a good moment to go back and revise it. But just to recap the basics, the state of such a system is anti-symmetric under exchange of any two particle indices. Thus we can write the general state as:

$$|\psi_{\mathbf{x}}\rangle = \frac{1}{\sqrt{N!}} \sum_{\mathbb{P}\in S_n} \text{sign}(\mathbb{P})\mathbb{P}|x_1, x_2, \ldots, , x_N\rangle \tag{8.11}$$

where $\text{sign}(\mathbb{P}) = -1$ if $\mathbb{P}$ involves an odd number of index swaps and $\text{sign}(\mathbb{P}) = 1$ if $\mathbb{P}$ involves an even number of index swaps. We note that given the Pauli exclusion principle, no two Fermions can be in the same state (i.e. $n_k = 1$ for all k), so each state in the sum here is unique and so the normalization is simply $\frac{1}{\sqrt{N!}}$.

Now, it'll be convenient here to switch notation and write this in terms of the wavefunctions explicitly. That is, we will work within the Hilbert space $\mathcal{H}_1$ of single-particle states, where the set $\{\phi_{n_i}\}_{i=1}^{N}$ represents an orthonormal basis of single-particle wave functions. Under these considerations, any wave function for N particles ψ can be expressed as:

$$\psi(x_1, \cdots, x_N) = \frac{1}{\sqrt{N!}} \sum_{\mathbb{P}\in S_n} \text{sign}(\mathbb{P})\mathbb{P}\phi_{n_1}(x_1) \quad \cdots\phi_{n_N}(x_N) \tag{8.12}$$

Or, equivalently, we can recognise this expression as a determinant and can write:

$$\psi(x_1, \cdots, x_N) = \frac{1}{N!} \begin{vmatrix} \phi_{n_1}(x_1) & \cdots & \phi_{n_N}(x_N) \\ \vdots & & \vdots \\ \phi_{n_N}(x_1) & \cdots & \phi_{n_N}(x_N) \end{vmatrix}. \tag{8.13}$$

We can now use our new found appreciation for the variational principle and can consider the ϕ_{n_i} as variational parameters. The Hartree-Fock approximation involves representing the ground state as a single Slater determinant, so we need to choose the ϕ_{n_i} that provide the best approximation.

The Hamiltonian of the system is given by $\hat{H} = \hat{T} + \hat{V}$, where

- The operator $\hat{T}$ is the total kinetic energy of the system, which is the sum of the kinetic energies of the N particles:
$$\hat{T} = \sum_{j=1}^{N} \hat{t}_j = \sum_{j=1}^{N} -\frac{\hbar}{2m}\nabla_j^2$$

- The operator $\hat{V}$ represents the potential energy of the N particles, given as the sum of potential energies of each pair of particles:
$$\hat{V} = \sum_{\substack{i,j \\ i\neq j}} \hat{V}_{i,j},$$
where $\hat{V}_{i,j} = \hat{V}(x_i, x_j)$.

We work within the Fock space. We have:

$$\langle\psi|\hat{T}|\psi\rangle = \sum_{j=1}^{N} \langle\phi_{n_j}|\hat{T}|\phi_{n_j}\rangle = \sum_{j=1}^{N} \int dx\phi_{n_j}^*(x)T(x)\phi_{n_j}(x), \tag{8.14}$$

and

$$\langle\psi|\hat{V}|\psi\rangle = \frac{1}{2}\sum_{i,j=1}^{N}\left(\langle\phi_{n_i}\phi_{n_j}|\hat{V}|\phi_{n_i}\phi_{n_j}\rangle - \langle\phi_{n_i}\phi_{n_j}|\hat{V}|\phi_{n_j}\phi_{n_i}\rangle\right) \tag{8.15}$$

$$= \frac{1}{2}\sum_{i,j=1}^{N}\int dx_1 dx_2\bigg(\phi^*_{n_i}(x_1)\phi^*_{n_j}(x_2)\hat{V}(x_1,x_2)\phi_{n_i}(x_1)\phi_{n_j}(x_2) \tag{8.16}$$

$$- \phi^*_{n_j}(x_1)\phi^*_{n_i}(x_2)\hat{V}(x_1,x_2)\phi_{n_i}(x_1)\phi_{n_j}(x_2)\bigg). \tag{8.17}$$

You should recognise this type of expression from when we studied indistinguishable particles - first term in the expression for $\langle\psi|\hat{V}|\psi\rangle$ is called the "direct term," while the second is the "exchange term."

The goal is to minimize $\langle\psi|\hat{H}|\psi\rangle = \langle\psi|\hat{T}|\psi\rangle + \langle\psi|\hat{V}|\psi\rangle$ subject to the N^2 constraints: $\langle\phi_{n_i}|\phi_{n_j}\rangle = \delta_{i,j}$. We use Lagrange multipliers to solve the constrained minimization problem.

Theorem 8.3.1 (Constrained Extrema via Lagrange multipliers)**.** *Seeking the extrema of a function $F(x,y)$ under a constraint $f(x,y) = 0$ is equivalent to searching for those of the function:*

$$H(x,y,\lambda) = F(x,y) - \lambda f(x,y).$$

Thus we are tasked with minimizing:

$$F = \langle\psi|\hat{H}|\psi\rangle - \sum_{i,j}\lambda_{i,j}\left(\langle\phi_{n_i}|\phi_{n_j}\rangle - \delta_{ij}\right). \tag{8.18}$$

We have N^2 constraints of the form $\langle\phi_{n_i}|\phi_{n_j}\rangle = \delta_{i,j}$ so initially it might seem that we need to introduce N^2 Lagrange multipliers. However, with a little thought we can see that the constraints with respect to swapping i and j and so it follows that $\lambda_{i,j} = \lambda^*_{i,j}$ which halves the number of constraints we need to deal with.

We consider ϕ and ϕ^* as independent variables. As an example, the variations with respect to $\phi^*_{n_i}$ yield:

$$\delta\hat{T} = \sum_j\int dx\delta\phi^*_{n_j}(x)\hat{t}\phi_{n_j}(x).$$

Similarly, the variations in $\hat{V}$ are:

$$\delta\hat{V} = \sum_{j\neq i}\int dx_1\int dx_2\bigg(\delta\phi^*_{n_i}(x_1)\phi^*_{n_j}(x_2)\hat{V}\phi_{n_i}(x_1)\phi_{n_j}(x_2) - \delta\phi^*_{n_i}(x_2)\phi^*_{n_j}(x_1)\hat{V}\phi_{n_i}(x_1)\phi_{n_j}(x_2)\bigg).$$

And the variations in the constraint term give:

$$\delta\sum_{i,j}\lambda_{i,j}\left(\langle\phi_{n_i}|\phi_{n_j}\rangle - 1\right) = \sum_{i,j}\lambda_{i,j}\int dx\delta\phi^*_i(x)\phi_j(x).$$

We want to minimize $F = \langle\psi|\hat{H}|\psi\rangle - \sum_{i,j}\lambda_{i,j}\left(\langle\phi_{n_i}|\phi_{n_j}\rangle - \delta_{ij}\right)$ with respect to ϕ_{n_i}. We, therefore, impose $\frac{\delta F}{\delta\phi^*_{n_i}} = 0$ for all i, which leads to the equation:

$$\hat{t}\phi_{n_i}(x) + \sum_{j=1}^{N}\int dx_2\bigg(\phi^*_{n_j}(x_2)\hat{V}\phi_{n_i}(x)\phi_{n_j}(x_2) - \phi^*_{n_j}(x)\hat{V}\phi_{n_i}(x)\phi_{n_j}(x_2)\bigg) = \sum_{j=1}^{N}\lambda_{i,j}\phi_{n_j}(x). \tag{8.19}$$

Without loss of generality we can chose to work in the basis in which the matrix λ is diagonal. That is, without loss of generality we can take $\lambda_{i,j} = \epsilon_i \delta_{i,j}$ and we end up with *the Hartree-Fock equation* :

$$-\frac{\hbar^2}{2m}\nabla^2\phi_{n_i}(x) + \sum_{j=1}^{N}\int dx_2 \bigg(\phi^*_{n_j}(x_2)\hat{V}\phi_{n_i}(x)\phi_{n_j}(x_2) - \phi^*_{n_j}(x)\hat{V}\phi_{n_i}(x)\phi_{n_j}(x_2)\bigg) = \epsilon_i\phi_{n_i}(x). \tag{8.20}$$

Or, equivalently, we can write this more compactly as:

$$\left(T(x) + V_H(x) - V_E(x)\right)\phi_{n_i}(x) = \epsilon_i\phi_{n_i}(x) \tag{8.21}$$

where we have defined

$$\begin{aligned} T(x) &:= -\frac{\hbar^2}{2m}\nabla^2 \\ V_H(x) &:= \sum_{j=1}^{N}\int dx_2 \phi^*_{n_j}(x_2)\hat{V}\phi_{n_j}(x_2) \\ V_E(x) &:= \sum_{j=1}^{N}\int dx_2 \phi^*_{n_j}(x)\hat{V}\phi_{n_j}(x_2)\,. \end{aligned} \tag{8.22}$$

Thus we see that we have decoupled the original eigenvalue problem defined on the N particle system into a set of N eigenvalue problems for each of the single particle states. This looks easier! The first term is the kinetic term, the second term is a potential energy term (which we will look at more closely in a second) and the third term is the 'exchange term' arising from the anti-symmetrization properties of the fermionic wave-function.

Ok, let us look more carefully at the $V_H(x)$ term (which corresponds to the direct integral term in the potential 8.17). Let's suppose that the potential has the form:

$$\hat{V}(x_1, x_2) = \frac{e^2}{|x_1 - x_2|} \tag{8.23}$$

We can then rewrite the Hartree term as:

$$\begin{aligned} \hat{V}_H(x) &= \sum_{j=1}^{N}\int dx_2 e^2 \frac{\left|\phi_{n_j}(x_2)\right|^2}{|x - x_2|} \\ &= e^2 \int dx_2 \frac{\sum_{j=1}^{N}\left|\phi_{n_j}(x)\right|^2}{|x - x_2|} \\ &= e^2 \int dx_2 \frac{\rho(x_2)}{|x - x_2|},. \end{aligned}$$

That is, the second term in the Hartree Fock equation can be interpreted as an effective potential generated by the average potential generated by surrounding particles. That is, the *Hartree potential energy is a functional of the density* $\rho(x)$, as ρ is a function of a single variable. Note, however, that the potential term depends on the wave-functions of all the other electrons.

If the exchange term V_E is negligible, then the initial N-body problem reduces to a one-body problem leading to the simplified Hartree equation:

$$-\frac{\hbar^2}{2m}\nabla^2\phi_{n_i}(x) + \hat{V}_H(x)\phi_{n_i}(x) = \epsilon_i\phi_{n_i}(x). \tag{8.24}$$

The Hartree energy is then given by:

$$E = \sum_{i=1}^{N} \langle \phi_{n_i} | \hat{t} | \phi_{n_i} \rangle + \int dx_1 \int dx_2 e^2 \frac{\rho(x_1)\rho(x_2)}{|x_1 - x_2|}. \tag{8.25}$$

While the Hartree equation has simplified the problem in the sense that we now have a set of equations for each of the one-body wavefunctions, solving these exactly is challenging as the potential term depends on the wavefunctions of all the particles via the density term $\rho(x)$. So to go further the general strategy is to pick a clever guess functional form for the density and then apply the variational principle. This is the core idea of what is known as *density functional theory* - a very powerful and widely used tool for approximating the energetic structure of many-body systems. At its core is the following Theorem:

Theorem 8.3.2 (First Hohenberg-Kohn Theorem)**.** *The energy E of the ground state of an N-particle system defined by $\hat{H}$ is an unknown functional of the density $\rho(x)$.*

If you are interested in knowing more on this I recommend Giuseppe Carleo's master's course on methods for simulating quantum systems.