Chapter 3

Approximation Methods in QM

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Basic Questions

A. What causes fine strucutre in hydrogen spectra?

B. What is Fermi's golden rule?

C. What is the variational principle?

3.1   Time-independent PT (nondegenerate)

3.1.1   Introduction

Two quantum problems can be solved exactly, they are harmonic oscillator and hydrogen (or hydrogen-like) atom. Most other quantum problems can not be solved exactly. One has to develop approximate method to solve such problem.

Consider a Hamiltonian $\hat{H}$, its Schrödinger eq.

$$\hat{H}\Psi_p = E_p\Psi_p, \quad p = \text{quantum no.}$$

is difficult to solve. If $\hat{H}$ can be written as

$$\hat{H} = \hat{H}_0 + \hat{V}$$

where $\hat{V}$ is time-independent and "small", and the Schrödinger eq. of $\hat{H}_0$ has been solved

$$\hat{H}_0\Phi_k = e_k\Phi_k \quad \rightarrow \quad \hat{H}_0\left|\Phi_k\right\rangle = e_k\left|\Phi_k\right\rangle$$

where k is the quantum number labelling the nondegenerate states. We wish to use the information of $\hat{H}_0$ to find the eigenstates and eigenvalues of $\hat{H}$. $\hat{H}_0$ is usually referred to as unperturbed Hamiltonian, $\hat{V}$ as perturbation potential (operator).

In principle (the completeness principle), any state Ψ_p can be written as a linear combination of Φ_k as

$$\left|\Psi_p\right\rangle = \sum_k C_{pk}\left|\Phi_k\right\rangle$$

where $\{C_{pk}\}$ are constants to be determined by eq. of $\hat{H}$, together with eigenvalue E_p. Since the dimensionality (total number of the possible k) is in general infinite, the exact solution is not easy. However, since the perturbation $\hat{V}$ is assumed small, it is not difficult to get approximate solution for $\left|\Psi_p\right\rangle$ and E_p.

3.1.2   Perturbation expansion

Obviously, if $\hat{V}$ is zero, $p = k$, $\left|\Psi_k\right\rangle = \left|\Phi_k\right\rangle$, $E_k = e_k$. Hence, for non-zero $\hat{V}$, this solution $\{p = k, \left|\Psi_k\right\rangle = \left|\Phi_k\right\rangle, E_k = e_k\}$ is referred to as **zero-order perturbation** results. We need to go beyond this, and find nontrivial correction to this zero-order results. In order to do it in a systematic way, we introduce a parameter λ in the Hamiltonian

$$\hat{H}\left(\lambda\right) = \hat{H}_0 + \lambda\hat{V}, \quad 0 \leq \lambda \leq 1$$

so that as $\lambda \rightarrow 0$, solutions for $\hat{H}\left(\lambda\right)$ is reduced to that of $\hat{H}_0$ and what we want is the results in the limit $\lambda = 1$. In perturbation theory, we assume

$$p = k$$

i.e., the quantum number for the states of $\hat{H}$ is same as that of $\hat{H}_0$. Therefore, we can expand each of the eigenvalues and eigenstates of $\hat{H}(\lambda)$ in terms of powers of λ as

$$
\begin{aligned}
E_k &= E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \lambda^3 E_k^{(3)} + \cdots \\
\Psi_k &= \Psi_k^{(0)} + \lambda \Psi_k^{(1)} + \lambda^2 \Psi_k^{(2)} + \lambda^3 \Psi_k^{(3)} + \cdots
\end{aligned}
$$

where $E_k^{(0)} = e_k$ is the zero-order approximation to the k-th eigenvalue of $\hat{H}$, and $E_k^{(1)}, E_k^{(2)}, E_k^{(3)}, \cdots$ are the successive correction to this. Similarly, $\Psi_k^{(0)} = \Phi_k$ is the zero-order appro. to k-th eigenstate of $\hat{H}$ and $\Psi_k^{(1)}, \Psi_k^{(2)}, \Psi_k^{(3)}, \cdots$ are the successive correction to this.

In order to find $E_k^{(1)}, E_k^{(2)}, E_k^{(3)}, \cdots$ and $\Psi_k^{(1)}, \Psi_k^{(2)}, \Psi_k^{(3)}, \cdots$, we substitute the expansions into the original Schrödinger eq.

$$
\hat{H}\Psi_k = E_k \Psi_k
$$

or

$$
\begin{aligned}
&\left(\hat{H}_0 + \lambda \hat{V}\right)\left(\Psi_k^{(0)} + \lambda \Psi_k^{(1)} + \lambda^2 \Psi_k^{(2)} + \cdots\right) \\
&= \left(E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \cdots\right)\left(\Psi_k^{(0)} + \lambda \Psi_k^{(1)} + \lambda^2 \Psi_k^{(2)} + \cdots\right)
\end{aligned}
$$

or, each side is arranged according to the powers of λ

$$
\begin{aligned}
&\hat{H}_0 \Psi_k^{(0)} + \lambda\left(\hat{V}\Psi_k^{(0)} + \hat{H}_0 \Psi_k^{(1)}\right) + \lambda^2\left(\hat{V}\Psi_k^{(1)} + \hat{H}_0 \Psi_k^{(2)}\right) + \cdots \\
&= E_k^{(0)}\Psi_k^{(0)} + \lambda\left(E_k^{(1)}\Psi_k^{(0)} + E_k^{(0)}\Psi_k^{(1)}\right) + \lambda^2\left(E_k^{(2)}\Psi_k^{(0)} + E_k^{(1)}\Psi_k^{(1)} + E_k^{(0)}\Psi_k^{(2)}\right) + \cdots
\end{aligned}
$$

Equating the coefficients of λ on both sides of the eq. (consider λ as an arbitrary number, this must be true), we have

$$
\hat{H}_0 \Psi_k^{(0)} = E_k^{(0)}\Psi_k^{(0)} \quad \rightarrow \quad \Psi_k^{(0)} = \Phi_k, \quad E_k^{(0)} = e_k
$$

as zero-order result, and

$$
\hat{V}\Psi_k^{(0)} + \hat{H}_0 \Psi_k^{(1)} = E_k^{(1)}\Psi_k^{(0)} + E_k^{(0)}\Psi_k^{(1)}
$$

as first-order eq. for $E_k^{(1)}$ and $\Psi_k^{(1)}$ and

$$
\hat{V}\Psi_k^{(1)} + \hat{H}_0 \Psi_k^{(2)} = E_k^{(2)}\Psi_k^{(0)} + E_k^{(1)}\Psi_k^{(1)} + E_k^{(0)}\Psi_k^{(2)}
$$

as second-order eq. for $E_k^{(2)}$ and $\Psi_k^{(2)}$ etc.

3.1.3   Solution for perturbation eq.: 1st-order

Now consider the solution to the above sequence of the perturbation eqs. The 1st-order eq. is

$$\hat{V}\Psi_k^{(0)} + \hat{H}_0\Psi_k^{(1)} = E_k^{(1)}\Psi_k^{(0)} + E_k^{(0)}\Psi_k^{(1)}$$

or, using the zero-order results

$$\left(\hat{V} - E_k^{(1)}\right)\Phi_k = \left(e_k - \hat{H}_0\right)\Psi_k^{(1)}$$

By the completeness principle, we can always express $\Psi_k^{(1)}$ in terms of a linear combination of Φ_k as

$$\Psi_k^{(1)} = \sum_{k'} C_{kk'}^{(1)}\Phi_{k'}$$

where $C_{kk'}^{(1)}$ are coefficients to be determined and the equation becomes, using $\hat{H}_0\Phi_{k'} = e_{k'}\Phi_{k'}$

$$\left(\hat{V} - E_k^{(1)}\right)\Phi_k = \sum_{k'}\left(e_k - e_{k'}\right)C_{kk'}^{(1)}\Phi_{k'}$$

$$\left(\hat{V} - E_k^{(1)}\right)|\Phi_k\rangle = \sum_{k'}\left(e_k - e_{k'}\right)C_{kk'}^{(1)}|\Phi_{k'}\rangle$$

this is the eq. for $E_k^{(1)}$ and $C_{kk'}$. The standard technique to solve this kind eq. is to take inner product with state $\Phi_{k''}$ on both sides of the eq., i.e., multiplying $\Phi_{k''}^*$ and integrate

$$\int d^3r\Phi_{k''}^*\left(\hat{V} - E_k^{(1)}\right)\Phi_k = \sum_{k'}\left(e_k - e_{k'}\right)C_{kk'}^{(1)}\int d^3r\Phi_{k''}^*\Phi_{k'}$$

using the orthonormal relation

$$\int d^3r\Phi_k^*\Phi_{k'} = \delta_{kk'}$$

we have

$$V_{k''k} - E_k^{(1)}\delta_{kk''} = \sum_{k'}\left(e_k - e_{k'}\right)C_{kk'}^{(1)}\delta_{k''k'} = \left(e_k - e_{k''}\right)C_{kk''}^{(1)}$$

$$V_{k''k} \equiv \int d^3r\Phi_{k''}^*\hat{V}\Phi_k$$

Choosing $k'' = k$ we have

$$E_k^{(1)} = V_{kk} = \int d^3r\Phi_k^*\hat{V}\Phi_k$$

Choosing $k'' \neq k$ we have

$$C_{kk''}^{(1)} = \frac{V_{k''k}}{e_k - e_{k''}} \; .$$

Note that C_{kk} is still undetermined and can be chosen as zero.

The 1st-order results are, letting $\lambda = 1$,

$$E_k \approx e_k + E_k^{(1)} = V_{kk} = \int d^3r \Phi_k^* \hat{V} \Phi_k$$

for the energy and

$$\Psi_k \approx \Phi_k + \sum_{k' \neq k} \frac{V_{k'k}}{e_k - e_{k'}} \Phi_{k'}$$

for the state. Note: if we choose $C_{kk} \neq 0$, the coefficient of Φ_k in the above formula will not be unity and Ψ_k is then not properly normalized in the limit $V_{k'k} \to 0$.

Note that the determine of the 1st-order energy $E_k^{(1)}$only depends on the zero-order state function $\Psi_k^{(0)} = \Phi_k$, and the 1st-order statefunction $\Psi_k^{(1)}$ is not necessary. However, in order to determine the 2nd -order energy correction $E_k^{(2)}$, the 1st-order statefunction correction $\Psi_k^{(1)}$ is required. This is generally true: nth-order energy correction requires the $(n-1)$th-order statefunction correction.

3.1.4 Solution for perturbation eq.: 2st-order

The 2nd-order equation is

$$\hat{V}\Psi_k^{(1)} + \hat{H}_0\Psi_k^{(2)} = E_k^{(2)}\Psi_k^{(0)} + E_k^{(1)}\Psi_k^{(1)} + E_k^{(0)}\Psi_k^{(2)}$$

or

$$E_k^{(2)}\Psi_k^{(0)} = \left(\hat{V} - E_k^{(1)}\right)\Psi_k^{(1)} + \left(\hat{H}_0 - E_k^{(0)}\right)\Psi_k^{(2)}$$

where $E_k^{(0)}, E_k^{(1)}, \Psi_k^{(0)}$ and $\Psi_k^{(1)}$ are known. We only need to determine $E_k^{(2)}$ and $\Psi_k^{(2)}$. Again, $\Psi_k^{(2)}$ can be written as a linear combination of Φ_k

$$\Psi_k^{(2)} = \sum_{k'} C_{kk'}^{(2)}\Phi_{k'}$$

substituting this into the eq., using the zero- and 1st-order results, we have

$$
\begin{aligned}
E_k^{(2)}\Phi_k &= \sum_{k'} C_{kk'}^{(1)}\left(\hat{V} - E_k^{(1)}\right)\Phi_{k'} + \sum_{k'} C_{kk'}^{(2)}\left(\hat{H}_0 - e_k\right)\Phi_{k'} \\
&= \sum_{k'} C_{kk'}^{(1)}\left(\hat{V} - E_k^{(1)}\right)\Phi_{k'} + \sum_{k'} C_{kk'}^{(2)}\left(e_{k'} - e_k\right)\Phi_{k'}
\end{aligned}
$$

as before, taking inner product with state $\Phi_{k''}$ on both sides of the eq. and using the orthonormality of Φ_k we have

$$E_k^{(2)}\delta_{k''k} = \sum_{k'} C_{kk'}^{(1)}\left(\hat{V}_{k''k'} - E_k^{(1)}\delta_{k''k'}\right) + C_{kk''}^{(2)}\left(e_{k''} - e_k\right) .$$

Choosing $k'' = k$, we obtain $E_k^{(2)}$

$$
\begin{aligned}
E_k^{(2)} &= \sum_{k'} C_{kk'}^{(1)}\left(V_{kk'} - E_k^{(1)}\delta_{kk'}\right) \\
&= \sum_{k'} C_{kk'}^{(1)}V_{kk'}, \quad \leftarrow \quad C_{kk}^{(1)} = 0 \\
&= \sum_{k'\neq k} \frac{V_{kk'}V_{k'k}}{e_k - e_{k'}} = \sum_{k'\neq k} \frac{|V_{kk'}|^2}{e_k - e_{k'}}
\end{aligned}
$$

where we have assume $\hat{V}$ is a Hermitian operator. The coefficient $C_{kk''}^{(2)}$ can be determined by choosing $k'' \neq k$, as before. Again, to determine $E_k^{(2)}$ we only need to know $C_{kk'}^{(1)}$ and $C_{kk''}^{(2)}$ is not necessary.

The 2nd-order result for the energy is then given by

$$
\begin{aligned}
E_k &\approx E_k^{(0)} + E_k^{(1)} + E_k^{(2)} = e_k + V_{kk} + \sum_{k'\neq k} \frac{|V_{kk'}|^2}{e_k - e_{k'}} \\
\Psi_k &\approx \Psi_k^{(0)} + \Psi_k^{(1)} = \Phi_k + \sum_{k'\neq k} \frac{V_{k'k}}{e_k - e_{k'}}\Phi_{k'}
\end{aligned}
$$

with

$$V_{k'k} \equiv \langle k'|\,\hat{V}\,|k\rangle = \int d^3r\, \Phi_{k'}^*\hat{V}\Phi_k .$$

3.1.5   Example

Consider an anharmonic oscillator with Hamiltonian

$$
\begin{aligned}
\hat{H} &= \hat{H}_0 + \hat{V} \\
\hat{H}_0 &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega x^2, \quad \hat{V} = \alpha x^3
\end{aligned}
$$

where α is a small number ($\alpha \ll \hbar\omega/x_0^3 = \hbar\omega\left(\frac{m\omega}{2\hbar}\right)^{3/2}$). The eigenequation of $\hat{H}_0$ has been solved,

$$
\begin{aligned}
\hat{H}_0\,|n\rangle &= \hbar\omega\left(n + \frac{1}{2}\right)|n\rangle, \quad n = 0, 1, 2, \cdots, \infty \\
\hat{H}_0 &= \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)
\end{aligned}
$$

and we know the effect of $\hat{a}^\dagger$ and $\hat{a}$ on the normalized state $|n\rangle$

$$\hat{a}^\dagger \, |n\rangle = \sqrt{n+1} \, |n+1\rangle \,, \quad \hat{a} \, |n\rangle = \sqrt{n} \, |n-1\rangle \quad \text{for } n > 0 \,.$$

we hence need to express $\hat{V}$ in terms of $\hat{a}$ and $\hat{a}^\dagger$. Using the definition

$$\hat{a} \equiv \sqrt{\frac{m\omega}{2\hbar}} \hat{x} + \frac{i\hat{p}}{\sqrt{2m\hbar\omega}}, \quad \hat{a}^\dagger \equiv \sqrt{\frac{m\omega}{2\hbar}} \hat{x} - \frac{i\hat{p}}{\sqrt{2m\hbar\omega}}$$

we have

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

hence

$$\begin{aligned}
\hat{V} &= \alpha \left(\frac{\hbar}{2m\omega} \right)^{3/2} \left(\hat{a} + \hat{a}^\dagger \right)^3 \\
&= \alpha \left(\frac{\hbar}{2m\omega} \right)^{3/2} \left(\hat{a} + \hat{a}^\dagger \right) \left(\hat{a}^2 + \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a} + \hat{a}^{\dagger 2} \right) \\
&= \alpha \left(\frac{\hbar}{2m\omega} \right)^{3/2} \left(\hat{a} + \hat{a}^\dagger \right) \left(\hat{a}^2 + 2\hat{a}^\dagger\hat{a} + 1 + \hat{a}^{\dagger 2} \right) \,.
\end{aligned}$$

Up to 2nd-order approximation, we have

$$E_n \approx e_n + V_{nn} + \sum_{n' \neq n} \frac{V_{nn'} V_{n'n}}{e_n - e_{n'}}$$

where

$$e_n = \hbar\omega \left(n + \frac{1}{2} \right)$$

and

$$\begin{aligned}
V_{nn} &= \langle n| \, \hat{V} \, |n\rangle \\
&= \alpha \left(\frac{\hbar}{2m\omega} \right)^{3/2} \langle n| \left(\hat{a} + \hat{a}^\dagger \right) \left(\hat{a}^2 + 2\hat{a}^\dagger\hat{a} + 1 + \hat{a}^{\dagger 2} \right) |n\rangle \\
&= \alpha \left(\frac{\hbar}{2m\omega} \right)^{3/2} \langle n| \left(\hat{a} + \hat{a}^\dagger \right) \left(\hat{a}^2 + 2n + 1 + \hat{a}^{\dagger 2} \right) |n\rangle \\
&= 0
\end{aligned}$$

i.e., the first-order energy correction is zero.

To determine the 2nd-order energy correction, we need to evaluate $V_{n'n}$. Consider

$$\left(\hat{a} + \hat{a}^\dagger\right)\left(\hat{a}^2 + 2\hat{a}^\dagger\hat{a} + 1 + \hat{a}^{\dagger 2}\right)|n\rangle$$

$$= \left(\hat{a} + \hat{a}^\dagger\right)\left(\hat{a}^2 + 2n + 1 + \hat{a}^{\dagger 2}\right)|n\rangle$$

$$= \left(\hat{a} + \hat{a}^\dagger\right)\left(\sqrt{n\left(n-1\right)}\,|n-2\rangle + \left(2n+1\right)|n\rangle + \sqrt{\left(n+1\right)\left(n+2\right)}\,|n+2\rangle\right)$$

$$= \sqrt{n\left(n-1\right)\left(n-2\right)}\,|n-3\rangle + \left(2n+1\right)\sqrt{n}\,|n-1\rangle + \sqrt{\left(n+1\right)\left(n+2\right)^2}\,|n+1\rangle$$
$$+ \sqrt{n\left(n-1\right)^2}\,|n-1\rangle + \left(2n+1\right)\sqrt{n+1}\,|n+1\rangle + \sqrt{\left(n+1\right)\left(n+2\right)\left(n+3\right)}\,|n+3\rangle$$

$$= \sqrt{n\left(n-1\right)\left(n-2\right)}\,|n-3\rangle + \left[\left(2n+1\right)\sqrt{n} + \sqrt{n\left(n-1\right)^2}\right]|n-1\rangle +$$
$$+ \left[\sqrt{\left(n+1\right)\left(n+2\right)^2} + \left(2n+1\right)\sqrt{n+1}\right]|n+1\rangle + \sqrt{\left(n+1\right)\left(n+2\right)\left(n+3\right)}\,|n+3\rangle$$

$$= \sqrt{n\left(n-1\right)\left(n-2\right)}\,|n-3\rangle + 3n^{3/2}\,|n-1\rangle + 3\left(n+1\right)^{3/2}\,|n+1\rangle$$
$$+ \sqrt{\left(n+1\right)\left(n+2\right)\left(n+3\right)}\,|n+3\rangle$$

therefore, there are only four nonzero contribution to $V_{n'n}$

$$V_{n-3,n} = \langle n-3|\,\hat{V}\,|n\rangle = \alpha\left(\frac{\hbar}{2m\omega}\right)^{3/2}\sqrt{n\left(n-1\right)\left(n-2\right)}$$

$$V_{n-1,n} = \langle n-1|\,\hat{V}\,|n\rangle = \alpha\left(\frac{\hbar}{2m\omega}\right)^{3/2}3n^{3/2}$$

$$V_{n+1,n} = \langle n+1|\,\hat{V}\,|n\rangle = \alpha\left(\frac{\hbar}{2m\omega}\right)^{3/2}3\left(n+1\right)^{3/2}$$

$$V_{n+3,n} = \langle n+3|\,\hat{V}\,|n\rangle = \alpha\left(\frac{\hbar}{2m\omega}\right)^{3/2}\sqrt{\left(n+1\right)\left(n+2\right)\left(n+3\right)}$$

therefore

$$\sum_{n'\neq n}\frac{V_{nn'}V_{n'n}}{e_n - e_{n'}} = \frac{V_{n-3,n}^2}{e_n - e_{n-3}} + \frac{V_{n-1,n}^2}{e_n - e_{n-1}} + \frac{V_{n+1,n}^2}{e_n - e_{n+1}} + \frac{V_{n+3,n}^2}{e_n - e_{n+3}}$$

$$= \frac{1}{3\hbar\omega}\alpha^2\left(\frac{\hbar}{2m\omega}\right)^3 n\left(n-1\right)\left(n-2\right)$$

$$+ \frac{1}{\hbar\omega}\alpha^2\left(\frac{\hbar}{2m\omega}\right)^3 9n^3$$

$$- \frac{1}{\hbar\omega}\alpha^2\left(\frac{\hbar}{2m\omega}\right)^3 9\left(n+1\right)^3$$

$$-\frac{1}{3\hbar\omega}\alpha^2\left(\frac{\hbar}{2m\omega}\right)^3(n+1)(n+2)(n+3)$$

$$= \frac{1}{3\hbar\omega}\alpha^2\left(\frac{\hbar}{2m\omega}\right)^3$$

$$\times\left[n(n-1)(n-2)+27n^3-27(n+1)^3-(n+1)(n+2)(n+3)\right]$$

$$= -\frac{1}{\hbar\omega}\alpha^2\left(\frac{\hbar}{2m\omega}\right)^3\left(30n^2+30n+11\right)$$

Hence, up to 2nd-order, the energy value is

$$E_n = \hbar\omega\left(n+\frac{1}{2}\right)-\frac{1}{\hbar\omega}\alpha^2\left(\frac{\hbar}{2m\omega}\right)^3\left(30n^2+30n+11\right)$$

and the energy interval between adjacent energy levels

$$\Delta = E_n - E_{n-1} = \hbar\omega - \frac{60}{\hbar\omega}\alpha^2\left(\frac{\hbar}{2m\omega}\right)^3 n$$

See figure

3.2 Degenerate PT

In the above perturbation theory, the unperturbed states Φ_k are nondegenerate, $e_{k'} \neq e_k$ for all $k' \neq k$. Now we extend the theory to the degenerate case. Our Hamiltonian is still given by

$$\hat{H} = \hat{H}_0 + \hat{V}$$

where the perturbed term $\hat{V}$ is assumed small and the unperturbed Hamiltonian $\hat{H}_0$ has been solved

$$\hat{H}_0\Phi_{nd} = e_n\Phi_{nd}$$

with quantum number $d = 1, 2, \cdots, M$, labelling the degeneracy. In the case of Hydrogen, we know for each n, we have degenerate qn $d = (l, m)$, $\sum_d = \sum_{l,m}$ and M^2. For convenience we only need one letter for the notation. We expect that the

introduction of perturbed term will lift the degeneracy in l, so the eigen equation for $\hat{H}$ is

$$\hat{H}\Psi_{nd} = E_{nd}\Psi_{nd} \ .$$

But if we still carry out the similar analysis as before, we expect to encounter a factor such as $\hat{H} \to \hat{H}(\lambda) = \hat{H}_0 + \lambda\hat{V}$, and the expansion series

$$\begin{aligned}
E_{nd} &= E_{nd}^{(0)} + \lambda E_{nd}^{(1)} + \cdots \\
\Psi_{nd} &= \Psi_{nd}^{(0)} + \lambda\Psi_{nd}^{(1)} + \cdots
\end{aligned}$$

substituting these into the original Schrödinger eq. and equating the coefficients of λ on both sides of the eq. (consider λ as an arbitrary number, this must be true), we have

$$\hat{H}_0\Psi_{nd}^{(0)} = E_{nd}^{(0)}\Psi_{n,d}^{(0)} \quad \to \quad \Psi_{nd}^{(0)} = \Phi_{nd}, \quad E_{nd}^{(0)} = e_n$$

as zero-order result, and

$$\hat{V}\Psi_{nd}^{(0)} + \hat{H}_0\Psi_{nd}^{(1)} = E_{nd}^{(1)}\Psi_{nd}^{(0)} + E_{nd}^{(0)}\Psi_{nd}^{(1)}$$

as first-order eq. etc. All those formulae remain the same, only replacing single qn by double ones $k \to (n,d)$. However, there are divergence problem when we go beyond zeroth-order. Consider the 1st-order correction to the wavefunction

$$\begin{aligned}
\Psi_{nd}^{(1)} &= \sum_{n'd'} c_{nd,n'd'}^{(1)}\Phi_{n'd'} \\
&= \sum_{d'\neq d} c_{nd,nd'}^{(1)}\Phi_{nd'} + \text{other contributions from states with } n' \neq n
\end{aligned}$$

with the diverging coefficient

$$c_{nd,nd'}^{(1)} = \frac{V_{nd,nd'}}{E_{nd}^{(0)} - E_{nd'}^{(0)}} = \frac{V_{nd,nd'}}{e_n - e_n} \ .$$

Solution: Recall the basic assumption in PT

quantum number after perturbation = quantum number before perturbation.

We need to modify this by introducing a new quantum number k as

$$\begin{aligned}
\text{before perturbation} &: \quad (n,d) \\
\text{after perturbation} &: \quad (n,k) \ .
\end{aligned}$$

This is equivalent to introduce a new basic set $\{\Omega_{nk}, k = 1, 2, \cdots, M\}$ as

$$\Omega_{nk} = \sum_{d=1}^{M} b_{kd}\Phi_{nd}, \quad k = 1, 2, \cdots, M$$

with coefficients b_{kd} to be determined by the condition to avoid the divergence mentioned above.

Now our new PT expansion series are

$$
\begin{aligned}
E_{nk} &= E_{nk}^{(0)} + \lambda E_{nk}^{(1)} + \cdots \\
\Psi_{nk} &= \Psi_{nk}^{(0)} + \lambda \Psi_{nk}^{(1)} + \cdots
\end{aligned}
$$

and the zeroth-order equation does not change much

$$
\hat{H}_0 \Psi_{nk}^{(0)} = E_{nk}^{(0)} \Psi_{nk}^{(0)} \rightarrow E_{nk}^{(0)} = e_n, \quad \Psi_{nk}^{(0)} = \Omega_{nk} = \sum_{d=1}^{M} b_{kd} \Phi_{nd}
$$

and the 1st-order eq.

$$
\left(\hat{V} - E_{nk}^{(1)} \right) \Psi_{nk}^{(0)} = \left(E_{nk}^{(0)} - \hat{H}_0 \right) \Psi_{nk}^{(1)}
$$

where we expand $\Psi_{nk}^{(1)}$ in terms of Ω_{nk}

$$
\Psi_{nk}^{(1)} = \sum_{k'} c_{kk'}^{(1)} \Omega_{nk'}, \quad k = 1, 2, \cdots, M .
$$

As before, we substitute this into the 1st-order eq. and take inner product with state $\Omega_{nk''}$ on both sides, we have

$$
\int d^3 r \, \Omega_{nk''}^* \left(\hat{V} - E_{nk}^{(1)} \right) \Omega_{nk} = \int d^3 r \, \Omega_{nk''}^* \sum_{k'} c_{kk'}^{(1)} \left(E_{nk}^{(0)} - \hat{H}_0 \right) \Omega_{nk'}
$$

or

$$
V_{nk'',nk} - E_{nk}^{(1)} \delta_{k''k} = \int d^3 r \, \Omega_{nk''}^* \sum_{k'} c_{kk'}^{(1)} \left(e_n - e_n \right) \Omega_{nk'} = 0 .
$$

Take $k'' = k$, we have

$$
E_{nk}^{(1)} = V_{nk,nk}
$$

and take $k'' \neq k$, we have

$$
V_{nk'',nk} = \int d^3 r \, \Omega_{nk''}^* \hat{V} \Omega_{nk} = 0, \quad \text{for all } k'' \neq k .
$$

This last equation means operator $\hat{V}$ is diagonal in the new basis. Therefore, the coefficients $\{b_{kd}\}$ in $\Omega_{nk} = \sum_{d=1}^{M} b_{kd} \Phi_{nd}$ is chosen so that $\hat{V}$ is diagonal.

Example: **Spin-orbit coupling (or *LS*-coupling)**. An electron moving in a central potential $\hat{V} = V(r)$ has Hamiltonian as

$$
\hat{H}_0 = -\frac{\hbar^2}{2m} \nabla^2 + V(r) .
$$

In general the eigenvalues E_{nl} of $\hat{H}_0$ are $2(2l+1)$-fold degenerate (for hydrogen, $E_{nl} = E_n$, and degeneracy is $2n^2$-fold). One of relativistic effects (Dirac) is the addition of a potential, the so-called spin-orbit coupling (or LS-coupling)

$$\hat{V}_{LS} = A(r)\,\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} .$$

We can treat this $\hat{V}_{LS}$ as perturbation potential and write

$$\hat{V}_{LS} = \frac{1}{2}A(r)\left(\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2\right), \quad \hat{\mathbf{J}} \equiv \hat{\mathbf{L}} + \hat{\mathbf{S}}$$

As we know, the eigenstates of $\hat{H}_0$ can be represented by the product of orbital wavefunctions and spin wavefunctions, or $|nlm\rangle |sm_s\rangle = |nlm_l sm_s\rangle$. Within the first-order degenerate PT, we need to use these $|nlm_l sm_s\rangle$ to diagonalize the perturbation operator $\hat{V}_{LS}$ and to obtain the zero-order wavefunction and first-order energy correction. We have already done so in the previous chapter. The zeroth-order wavefunction are angular momentum states $|nlsjm\rangle$ which are eigenstates of $\hat{\mathbf{J}}^2$ and $\hat{J}_z$ with angular momentum quantum number, using $s = 1/2$

$$j = l \pm \frac{1}{2}, \quad m = -j, -j+1, \cdots, j-1, j .$$

Hence, the energy level shift by LS-coupling is

$$E_{LS}^{(1)} = \langle nlsjm| \hat{V}_{LS} |nlsjm\rangle = \frac{\hbar^2}{2}\left[j(j+1) - l(l+1) - \frac{3}{4}\right]\langle A(r)\rangle_{nl} .$$

3.3   Time-dependent perturbation theory

3.3.1   Newton's equation

As we have seen before, the time-dependent Schrödinger eq. is

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \hat{H}\Psi(\mathbf{r},t), \quad -i\hbar\frac{\partial}{\partial t}\Psi^*(\mathbf{r},t) = \hat{H}\Psi^*(\mathbf{r},t) .$$

The expectation value of an arbitrary operator $\hat{A} = \hat{A}(t)$, assumed $\Psi(\mathbf{r},t)$ is normalized,

$$\left\langle \hat{A} \right\rangle = \langle \Psi| \hat{A} |\Psi\rangle = \int d^3r\, \Psi^*(\mathbf{r},t)\,\hat{A}(t)\,\Psi(\mathbf{r},t)$$

has the following evolution equation

$$\begin{aligned}
\frac{d}{dt}\left\langle \hat{A} \right\rangle &= \int d^3r\, \frac{\partial}{\partial t}\left[\Psi^*(\mathbf{r},t)\,\hat{A}(t)\,\Psi(\mathbf{r},t)\right] \\
&= \int d^3r\, \Psi^*(\mathbf{r},t)\frac{\partial \hat{A}}{\partial t}\Psi(\mathbf{r},t) + \frac{1}{i\hbar}\int d^3r\, \Psi^*(\mathbf{r},t)\left(\hat{A}\hat{H} - \hat{H}\hat{A}\right)\Psi(\mathbf{r},t)
\end{aligned}$$

or

$$\frac{d}{dt}\left\langle \hat{A} \right\rangle = \left\langle \frac{\partial \hat{A}}{\partial t} \right\rangle + \frac{1}{i\hbar}\left\langle \left[\hat{A},\ \hat{H} \right] \right\rangle .$$

Using this formula, Newton's equation becomes, using $\hat{H} = \hat{p}^2/2m + \hat{V}(\mathbf{r})$

$$\frac{d}{dt}\langle \hat{\mathbf{p}} \rangle = -\left\langle \nabla \hat{V} \right\rangle .$$

3.3.2 Time-dependent expansion

Consider now the following Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{V}(t)$$

where $\hat{H}_0$ is time-independent with eigen eqs.

$$\hat{H}_0 \Phi_n(\mathbf{r}) = E_n \Phi_n(\mathbf{r}), \quad n = 1, 2, \cdots$$

and the time dependent part of the Hamiltonian is $\hat{V}(t)$. The general time-dependent wavefunction $\Psi(\mathbf{r}, t)$ can be expanded in the following general form as

$$\Psi(\mathbf{r}, t) = \sum_n d_n(t)\, \Phi_n(\mathbf{r}) = \sum_n c_n(t)\, \Phi_n(\mathbf{r})\, e^{-iE_n t/\hbar}$$

and after substituting into the Schrödinger eq., we have

$$\sum_n \left(E_n c_n + i\hbar \frac{dc_n}{dt} \right) \Phi_n(\mathbf{r})\, e^{-iE_n t/\hbar} = \sum_n \left(E_n + \hat{V} \right) c_n \Phi_n(\mathbf{r})\, e^{-iE_n t/\hbar}$$

or

$$i\hbar \sum_{n'} \frac{dc_{n'}}{dt} \Phi_{n'}(\mathbf{r})\, e^{-iE_{n'} t/\hbar} = \sum_{n'} c_{n'} \hat{V} \Phi_{n'}(\mathbf{r})\, e^{-iE_{n'} t/\hbar} .$$

Taking inner product with $\Phi_n(\mathbf{r})$ on both sides of eq., we have the time-evolution equation for $c_n(t)$

$$i\hbar \frac{dc_n}{dt} = \sum_{n'} V_{nn'} c_{n'} e^{i\omega_{nn'} t}, \quad n = 1, 2, \cdots$$

with

$$V_{nn'} \equiv \langle \Phi_n | \hat{V} | \Phi_{n'} \rangle = \int d^3 r\, \Phi_n^* \hat{V} \Phi_{n'}, \quad \hbar\omega_{nn'} = E_n - E_{n'} .$$

these are a set of first-order, coupled equations for $\{c_n, n = 1, 2, \cdots\}$. Normally difficult to solve. For some special case, exact solution can be found. See Mandl, *Quantum Mechanics*, Section 9.2, P 198.

Consider a typical initial condition: at $t = 0$, the system is in one of the eigenstate, say, $|1\rangle$, namely

$$c_n(0) = \delta_{1n} \, .$$

For $\hat{V}(t) = 0$, the amplitudes $c_n(t)$ retain this initial value at all times and

$$\Psi(\mathbf{r}, t) = \sum_n c_n(t) \, \Phi_n(\mathbf{r}) \, e^{-iE_n t/\hbar} = \Phi_1(\mathbf{r}) \, e^{-iE_1 t/\hbar}$$

the time-dependent part is trivial.

3.3.3   Perturbation Theory

Now we treat $\hat{V}$ as perturbation potential and write the Hamiltonian as before

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}(t)$$

and correspondingly

$$c_n = c_n^{(0)} + \lambda c_n^{(1)} + \lambda^2 c_n^{(2)} + \cdots$$

the evolution equation for c_n becomes

$$i\hbar \frac{d}{dt}\left(c_n^{(0)} + \lambda c_n^{(1)} + \lambda^2 c_n^{(2)} + \cdots\right) = \sum_{n'}\left(c_{n'}^{(0)} + \lambda c_{n'}^{(1)} + \lambda^2 c_{n'}^{(2)} + \cdots\right)\lambda V_{nn'} e^{i\omega_{nn'}t} \, .$$

Setting the coefficients of each power of λ equal on both sides we have a series successive eqs.,

$$
\begin{aligned}
i\hbar \frac{d}{dt}c_n^{(0)} &= 0, \quad c_n^{(0)}(t) = \text{const.} \\
i\hbar \frac{d}{dt}c_n^{(1)} &= \sum_{n'} c_{n'}^{(0)} V_{nn'} e^{i\omega_{nn'}t} \\
i\hbar \frac{d}{dt}c_n^{(2)} &= \sum_{n'} c_{n'}^{(1)} V_{nn'} e^{i\omega_{nn'}t} \\
&\cdots \, .
\end{aligned}
$$

Consider the typical initial condition: applying the perturbation $\hat{V}(t)$ after $t > 0$, namely

$$\hat{V}(t)\begin{cases} = 0, & t \le 0 \\ \ne 0, & t > 0 \end{cases}$$

and assume for $t \le 0$, the system is in one of the eigenstates of $\hat{H}_0$, say $|1\rangle$,

$$c_n(0) = c_n^{(0)}(t) = \delta_{1n}$$

Hence the first-order equation becomes

$$ i\hbar \frac{d}{dt} c_n^{(1)} = \sum_{n'} c_{n'}^{(0)} V_{nn'} e^{i\omega_{nn'}t} = V_{n1} e^{i\omega_{n1}t} $$

Integrating these equations from $t = 0$ to $t > 0$, subject to the condition that $c_n(0) = \delta_{1n}$, we have

$$ c_1^{(1)}(t) = 1 + \frac{1}{i\hbar} \int_0^t \hat{V}_{11}(t')\,dt' $$

$$ c_n^{(1)}(t) = \frac{1}{i\hbar} \int_0^t \hat{V}_{n1}(t')\, e^{i\omega_{n1}t'}\,dt', \quad \omega_{n1} = \frac{E_n - E_1}{\hbar}, \quad n \neq 1 $$

where $\left| c_1^{(1)}(t) \right|^2$ is the probability (in 1st-order approximation) that the system at $t > 0$ stays in the original state $|1\rangle$, and $\left| c_n^{(1)}(t) \right|^2$ is the probability (in 1st-order approximation) that the system at $t > 0$ is in another state $|n\rangle$ ($n \neq 1$).

   Example. A hydrogen atom is placed in a spatially homogeneous time-dependent electric field in the z-axis

$$ \varepsilon = \begin{cases} 0, & t \leq 0 \\ \varepsilon_0 e^{-t/\tau}, & t > 0 \end{cases} $$

with $\tau > 0$. At time $t = 0$, the atom is in the $(1s)$ ground state with wavefunction and energy

$$ \phi_{1s} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}, \quad E_{1s} = -\frac{e^2}{8\pi\epsilon_0 a_0}, \quad a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2}. $$

Find the probability, in the 1st order perturbation theory, that after a sufficiently long time the atom is in the $(2p)$ excited state with wavefunction and energy

$$ \phi_{2p} = \frac{1}{\sqrt{32\pi a_0^5}} r \cos\theta\, e^{-r/2a_0}, \quad E_{2p} = \frac{E_{1s}}{4}. $$

   Solution: According to the 1st-order perturbation theory, the probability amplitude for the transition $(1s) \to (2p)$ is

$$ c(t) = \frac{1}{i\hbar} \int_0^t \hat{V}_{2p,1s}(t')\, e^{i\omega_{2p,1s}t'}\,dt' $$

with

$$ \omega_{2p,1s} = \frac{E_{2p} - E_{1s}}{\hbar} = -\frac{3E_{1s}}{4\hbar} $$

and

$$ \hat{V}(t') = e\varepsilon_0 e^{-t'/\tau} z = e\varepsilon_0 e^{-t'/\tau} r\cos\theta. $$

The matrix element $\hat{V}_{2p,1s}(t')$ is

$$
\begin{aligned}
\hat{V}_{2p,1s}(t') &= \langle 2p|\,\hat{V}(t')\,|1s\rangle = e\varepsilon_0 e^{-t'/\tau}\,\langle 2p|\,r\cos\theta\,|1s\rangle \\
&= e\varepsilon_0 e^{-t'/\tau}\int\left(\frac{1}{\sqrt{32\pi a_0^5}}r\cos\theta\,e^{-r/2a_0}\cdot\frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}\right)r^2\sin\theta\,dr\,d\theta\,d\phi \\
&= e\varepsilon_0 e^{-t'/\tau}\frac{1}{4\sqrt{2}\pi a_0^4}\left(\int_0^\infty r^4 e^{-3r/2a_0}\,dr\right)\left(\int_0^\pi \cos^2\theta\sin\theta\,d\theta\right)\left(\int_0^{2\pi}d\phi\right) \\
&= e\varepsilon_0 e^{-t'/\tau}\frac{1}{4\sqrt{2}\pi a_0^4}\cdot\frac{4!2^5 a_0^5}{3^5}\cdot\frac{2}{3}\cdot 2\pi = Ce^{-t/\tau},\quad C\equiv\frac{2^{15/2}}{3^5}e\varepsilon_0 a_0
\end{aligned}
$$

and the amplitude

$$
c(t) = \frac{C}{i\hbar}\int_0^t e^{i\omega_{2p,1s}t'-t'/\tau}\,dt' = \frac{C}{i\hbar}\frac{e^{i\omega_{2p,1s}t-t/\tau}-1}{i\omega_{2p,1s}-1/\tau}
$$

and the transition probability is

$$
|c(t)|^2 = \frac{C^2}{\hbar^2}\frac{1+e^{-2t/\tau}-2e^{-t/\tau}\cos(\omega_{2p,1s}t)}{\omega_{2p,1s}^2+1/\tau^2},
$$

and after a sufficiently long time, $t=\infty$, the probability is

$$
|c(\infty)|^2 = \frac{2^{15}}{3^{10}}\frac{(e\varepsilon_0 a_0)^2}{(3E_{1s}/4)^2+(\hbar/\tau)^2}\,.
$$

3.3.4   Fermi golden rule

Now we consider the following simpler case, a step function perturbation potential

$$
\hat{V}(t) = \begin{cases} 0, & t\le 0 \\ \hat{V}, & t>0 \end{cases}
$$

where $\hat{V}$ is independent of time. What is the **transition probability per unit time** for the system originally in state $|1\rangle$ at $t\le 0$ to the state $|2\rangle$ at $t>0$?

   Solution: From the above 1sr-order perturbation theory, the time-integration in the transition probability amplitude can be carried out,

$$
\begin{aligned}
c^{(1)}_{2\leftarrow 1}(t) &= \frac{1}{i\hbar}\int_0^t V_{2,1}(t')\,e^{i\omega_{2,1}t'}\,dt' = \frac{V_{2,1}}{\hbar\omega_{2,1}}\left(1-e^{i\omega_{2,1}t}\right) \\
V_{2,1} &= \langle 2|\,\hat{V}\,|1\rangle,\quad \omega_{2,1}=\frac{E_2-E_1}{\hbar}
\end{aligned}
$$

and the probability is, using $\sin y = (e^{iy} - e^{-iy})/2$,

$$P_{2\leftarrow 1}(t) = \left|c_{2\leftarrow 1}^{(1)}(t)\right|^2 = \frac{4\,|V_{2,1}|^2}{\hbar^2}\frac{\sin^2(\omega_{2,1}t/2)}{\omega_{2,1}^2} = \frac{2\pi t}{\hbar^2}\,|V_{2,1}|^2\,D(\omega_{2,1},t)$$

$$D(x,t) = \frac{2}{\pi t}\frac{\sin^2(xt/2)}{x^2}, \quad x = \omega_{2,1}$$

where function $D(x,t)$ has a simple integral

$$\int_{-\infty}^{\infty} D(x,t)\,dx = \frac{2}{\pi t}\int_{-\infty}^{\infty}\frac{\sin^2(xt/2)}{x^2}dx = 1, \quad \text{using} \int_{-\infty}^{\infty}\frac{\sin^2(ax)}{x^2}\,dx = \pi a,$$

similar to the continuous delta function $\delta(x)$. In the limit $t \to \infty$, the two become identical. So we have the transition probability given by, for large t

$$P_{2\leftarrow 1}(t) = \frac{2\pi t}{\hbar^2}\,|V_{2,1}|^2\,\delta(\omega_{2,1}) = \frac{2\pi t}{\hbar}\,|V_{2,1}|^2\,\delta(E_2 - E_1)$$

and the probability per unit time

$$\dot{P}_{2\leftarrow 1}(t) = \frac{2\pi}{\hbar}\,|V_{2,1}|^2\,\delta(E_2 - E_1)\ .$$

This is the famous Fermi Golden rule.

3.4 Variational method

3.4.1 Variational principle

Variational principle (Rayleigh-Ritz): The expectation value of a given Hamiltonian $\hat{H}$ in any state Ψ is always greater or equal to the exact ground-state energy E_0,

$$\frac{\langle\Psi|\,\hat{H}\,|\Psi\rangle}{\langle\Psi\,|\Psi\rangle} \geq E_0$$

the equality holds if $|\Psi\rangle$ is the exact ground state.

Proof: Suppose

$$\hat{H}\,|\Phi_n\rangle = E_n\,|\Phi_n\rangle, \quad n = 0, 1, 2, \cdots$$
$$E_0 < E_n, \quad \text{for } n > 0$$

Write $|\Psi\rangle$ as a linear combination of $|\Phi_n\rangle$

$$|\Psi\rangle \;=\; \sum_{n=0}^{\infty} C_n |\Phi_n\rangle = C_0 |\Phi_0\rangle + \sum_{n=1}^{\infty} C_n |\Phi_n\rangle$$

$$\langle \Psi\,|\,\Psi\rangle \;=\; |C_0|^2 + \sum_{n=1}^{\infty} |C_n|^2$$

Therefore

$$\hat{H}\,|\Psi\rangle \;=\; \hat{H}\left(C_0 |\Phi_0\rangle + \sum_{n=1}^{\infty} C_n |\Phi_n\rangle\right)$$

$$=\; E_0 C_0 |\Phi_0\rangle + \sum_{n=1}^{\infty} C_n E_n |\Phi_n\rangle$$

and

$$\langle\Psi|\,\hat{H}\,|\Psi\rangle \;=\; E_0 |C_0|^2 + \sum_{n=1}^{\infty} E_n |C_n|^2$$

$$>\; E_0 |C_0|^2 + E_0 \sum_{n=1}^{\infty} |C_n|^2 = E_0\left(|C_0|^2 + \sum_{n=1}^{\infty} |C_n|^2\right) = E_0 \langle\Psi\,|\,\Psi\rangle$$

so

$$\frac{\langle\Psi|\,\hat{H}\,|\Psi\rangle}{\langle\Psi\,|\,\Psi\rangle} \geq E_0\ .$$

In general, we do not know the exact ground state energy E_0. We wish to find an approximation for its value. By the variational principle, our approximation $\langle\hat{H}\rangle$ using any trial wavefunction $|\Psi\rangle$ will always be greater than the exact value E_0. Hence, the lower the expectation value $\langle\hat{H}\rangle$ (i.e., the closer to the exact value), the better the trial wavefunction. A typical varitaional calculation is as follows: we first choose a trial wavefunction Ψ with a few variational parameters $\alpha_1, \alpha_2, \cdots$

$$\Psi\,(\alpha_1, \alpha_2, \cdots)$$

and calculate the expectation value

$$E\,(\alpha_1, \alpha_2, \cdots) = \frac{\langle\Psi|\,\hat{H}\,|\Psi\rangle}{\langle\Psi\,|\,\Psi\rangle}.$$

Next, we minimize this $E\,(\alpha_1, \alpha_2, \cdots)$ through variational equations

$$\frac{\partial}{\partial\alpha_1} E\,(\alpha_1, \alpha_2, \cdots) \;=\; 0$$

$$\frac{\partial}{\partial\alpha_2} E\,(\alpha_1, \alpha_2, \cdots) \;=\; 0$$

$$\cdots$$

The solution for $(\alpha_1, \alpha_2, \cdots)$ of these equations then put back to $E(\alpha_1, \alpha_2, \cdots)$ and this minimum E represents the best estimate for the trial function of the form $\Psi(\alpha_1, \alpha_2, \cdots)$.

Clearly, the success of this nonperturbative method will depend crucially on the form of the trial wave functions we choose to start with.

3.4.2 Examples

Hydrogen atom. The trial function for the ground state of Hydrogen is choose as

$$\Phi_\alpha = Ce^{-\alpha r}, \quad C = \sqrt{\frac{\alpha^3}{\pi}}$$

the Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}, \quad \nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\hat{A}(\theta\phi)$$

and the expectation value is

$$E_\alpha = \langle\Phi_\alpha|\,\hat{H}\,|\Phi_\alpha\rangle = \frac{\hbar^2\alpha^2}{2m} - \frac{e^2\alpha}{4\pi\epsilon_0}$$

hence

$$\frac{\partial E_\alpha}{\partial \alpha} = 0 \quad \to \quad \alpha = \frac{e^2 m}{4\pi\epsilon_0 \hbar^2} = \frac{1}{a_0}$$

where a_0 is the Bohr radius. So the best estimate for the ground state energy is

$$E_\alpha = \frac{\hbar^2}{2m}\frac{1}{a_0^2} - \frac{e^2\alpha}{4\pi\epsilon_0}\frac{1}{a_0} = -\frac{1}{2}\frac{e^2}{4\pi\epsilon_0 a_0}$$

and for the ground state is

$$\Phi = \frac{1}{\sqrt{a_0^3\pi}}e^{-r/a_0}$$

both are actually exact. This is not surprising because the trial function has the correct form.

Helium atom. In this case we do not know the exact result and we are dealing with two identical particles. Consider in general Helium-like ions with the following Hamiltonian describing two electrons interacting each other and with a nucleus containing Z protons

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}}\,.$$

We want to approximate the ground state of this system by a simple trial wavefunction (actually, PT), using the knowledge from hydrogen-like ions.

We know the eigenstates $\phi_{nlm}(\mathbf{r})$ for a single electron $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r}$ are

$$
\begin{aligned}
\phi_{1s}(\mathbf{r}) &= R_{10}(r)Y_{00}(\theta,\phi) = \sqrt{\frac{Z^3}{\pi a_0^3}}e^{-Zr/a_0} \\
\phi_{2s}(\mathbf{r}) &= R_{20}(r)Y_{00}(\theta,\phi) = \sqrt{\frac{Z^3}{8\pi a_0^3}}\left(1 - \frac{Zr}{2a_0}\right)e^{-Zr/a_0} \\
&\quad\cdots
\end{aligned}
$$

with $\phi_{1s}(\mathbf{r})$ as the ground state, and eigenvalues

$$
E_{nl} = E_n = -\frac{e^2}{8\pi\epsilon_0 a_0}\frac{Z^2}{n^2}, \quad n = 1, 2, \cdots \quad .
$$

We also know electrons have spin degree of freedom, indicated by two states $|\uparrow\rangle$ or $|\downarrow\rangle$. We want to construct the simplest two-body wavefunction from these single-body state. There is a (anti)symmetry requirement we need to impose. The following is a trial wavefunction satisfying this requirement,

$$
\Psi_0(1,2) = \phi_{1s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)\chi_{12}, \quad \chi_{12} = \frac{1}{\sqrt{2}}\left(|\uparrow\rangle_1|\downarrow\rangle_2 - |\downarrow\rangle_1|\uparrow\rangle_2\right)
$$

hence $\Psi(1,2) = -\Psi(2,1)$. This is a spin-singlet state. Another possible trial state is the spin-triplet,

$$
\begin{aligned}
\Psi_0'(1,2) &= \frac{1}{\sqrt{2}}\left[\phi_{1s}(\mathbf{r}_1)\phi_{2s}(\mathbf{r}_2) - \phi_{2s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)\right]\tau_{12}, \\
\tau_{12} &= |\uparrow\rangle_1|\uparrow\rangle_2, \quad \frac{1}{\sqrt{2}}\left(|\uparrow\rangle_1|\downarrow\rangle_2 + |\downarrow\rangle_1|\uparrow\rangle_2\right), \quad |\downarrow\rangle_1|\downarrow\rangle_2
\end{aligned}
$$

but this will give higher energy due to the present of the higher level state $\phi_{2s}(\mathbf{r}_1)$. (It is quite easy to test experimentally if the ground state Helium is singlet or triplet.) Using the singlet state $\Psi_t(1,2)$, we evaluate the energy expectation value

$$
\begin{aligned}
\langle\hat{H}\rangle &= 2\cdot\left\langle\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r_1}\right\rangle + \frac{e^2}{4\pi\epsilon_0}\left\langle\frac{1}{r_{12}}\right\rangle \\
&= 2\cdot\left(-\frac{Z^2e^2}{8\pi\epsilon_0 a_0}\right) + \frac{5}{4}\frac{Ze^2}{8\pi\epsilon_0 a_0} \\
&= \left(-2Z^2 + \frac{5}{4}Z\right)\text{Ry}, \quad \text{Ry} = \frac{e^2}{8\pi\epsilon_0 a_0} \\
&= -5.50\text{ Ry}, \quad Z = 2
\end{aligned}
$$

which is only 6% above the experimental result of -5.81 Ry.

Math Note: Evaluate $\left\langle \frac{1}{r_{12}} \right\rangle$:

$$\left\langle \frac{1}{r_{12}} \right\rangle = \frac{1}{\pi^2} \left(\frac{Z}{a_0} \right)^6 \int d^3r_1 d^3r_1 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} e^{-2Z(r_1+r_2)/a_0} \ .$$

First we use the expression (Fourier transformation)

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \int \frac{d^3k}{(2\pi)^3} e^{i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)} \frac{4\pi}{k^2}$$

hence

$$\left\langle \frac{1}{r_{12}} \right\rangle = \frac{1}{\pi^2} \left(\frac{Z}{a_0} \right)^6 \int \frac{d^3k}{(2\pi)^3} \frac{4\pi}{k^2} \left| \int d^3r_1 e^{i\mathbf{k}\cdot\mathbf{r}_1 - 2Zr_1/a_0} \right|^2$$

now

$$\int d^3r_1 e^{i\mathbf{k}\cdot\mathbf{r}_1 - 2Zr_1/a_0} = \frac{16\pi Z/a_0}{\left[k^2 + (2Z/a_0)^2 \right]^2}$$

and finally

$$\left\langle \frac{1}{r_{12}} \right\rangle = \frac{4Z}{\pi a_0} \int_0^\infty \frac{dx}{(x^2+1)^4} = \frac{5}{8} \frac{Z}{a_0} \ .$$

We can improve our wavefunction by introducing a variational parameter Z'

$$\phi_{1s}\left(\mathbf{r}\right) = \sqrt{\frac{Z'^3}{\pi a_0^3}}e^{-Z'r/a_0}, \quad \Psi_0\left(1,2\right) = \phi_{1s}\left(\mathbf{r}_1\right)\phi_{1s}\left(\mathbf{r}_2\right)\chi_{12}$$

and repeat our calculation as before, see example one,

$$\begin{aligned}
\left\langle\hat{H}\right\rangle_{Z'} &= 2\cdot\left\langle\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r_1}\right\rangle_{Z'} + \frac{e^2}{4\pi\epsilon_0}\left\langle\frac{1}{r_{12}}\right\rangle_{Z'} \\
&= 2\cdot\left(\frac{Z'^2e^2}{8\pi\epsilon_0 a_0} - \frac{ZZ'e^2}{4\pi\epsilon_0 a_0}\right) + \frac{5}{4}\frac{Z'e^2}{8\pi\epsilon_0 a_0} \\
&= 2\left(Z'^2 - 2Z'Z + \frac{5}{8}Z'\right)\text{ Ry}, \quad \text{Ry} = \frac{e^2}{8\pi\epsilon_0 a_0}
\end{aligned}$$

and variational eq.

$$\frac{\partial}{\partial Z'}\left\langle\hat{H}\right\rangle_{Z'} = 0 \rightarrow Z' = Z - \frac{5}{16}$$

and the estimated ground-state energy

$$\begin{aligned}
\left\langle\hat{H}\right\rangle_{Z'=Z-5/16} &= -2\left(Z - \frac{5}{16}\right)^2\text{ Ry}, \quad Z = 2 \\
&= -\frac{2\cdot 27^2}{16^2}\text{ Ry} = -5.70\text{ Ry}
\end{aligned}$$

which is closer to the experimental result of -5.81 Ry. (higher no more than 2%). Physically, the variational parameter Z' represents the mutual screening by the two electrons.

Now how does one go from here? Can we further improve our estimate and how? A more sophisticated variational wavefunction (Hylleraas) is

$$\begin{aligned}
\Psi\left(1,2\right) &= P\left(s,t,u\right)\Psi_0\left(1,2\right) \\
s &\equiv \frac{Z'}{a_0}\left(r_1 + r_2\right), \quad t \equiv \frac{Z'}{a_0}\left(r_1 - r_2\right), \quad u \equiv \frac{Z'}{a_0}r_{12}
\end{aligned}$$

where $P\left(s,t,u\right)$ is expanded in power series of s, t and u

$$P\left(s,t,u\right) = \sum_{l,n,m} c_{n,2l,m}s^n t^{2l} u^m$$

and variational eqs. are

$$\frac{\partial}{\partial c_{n,2l,m}}\left\langle\hat{H}\right\rangle = 0, \quad \frac{\partial}{\partial Z'}\left\langle\hat{H}\right\rangle = 0$$

and by including 10 $c_{n,2l,m}$ parameters, the accuracy can reach to 6-7 digits. See *Intermediate QM*, 1964, H.A. Bethe.

Variational method and diagonalization. For a given basis set (truncated or untruncated), $\{|n\rangle, n = 1, 2, \cdots, N\}$, the trial wavefunction can be written as

$$|\Psi\rangle = \sum_{n=1}^{N} c_n |n\rangle, \quad \langle\Psi| = \sum_{n=1}^{N} \langle n| c_n^*$$

where $\{c_n^*, c_n; n = 1, 2, \cdots, N\}$ are variational parameters determined by

$$\frac{\delta}{\delta c_n^*} \left\langle \hat{H} \right\rangle = \frac{\delta}{\delta c_n} \left\langle \hat{H} \right\rangle = 0, \quad \left\langle \hat{H} \right\rangle = \frac{\langle\Psi| \hat{H} |\Psi\rangle}{\langle\Psi |\Psi\rangle}$$

or

$$\frac{\langle\Psi |\Psi\rangle \sum_{n'=1}^{N} H_{nn'} c_{n'} - \langle\Psi| \hat{H} |\Psi\rangle c_n}{\langle\Psi |\Psi\rangle^2} = 0, \quad H_{nn'} \equiv \langle n| \hat{H} |n'\rangle$$

or

$$\sum_{n'=1}^{N} H_{nn'} c_{n'} = \left\langle \hat{H} \right\rangle c_n, \quad n = 1, 2, \cdots, N .$$

This is precisely the eigenequation for the Hamiltonian matrix $\{H_{nn'}\}$ with the energy eigenvalue $\left\langle \hat{H} \right\rangle$. Therefore, the variational method and diagonalization is equivalent.