VI.) Approximation Methods For Bound States

There are very few situations in which we can solve Schrödinger's equation exactly. Hence approximation techniques form an important tool in analyzing physical systems. The general idea of these approximations is that the bulk of the properties of a system we can determine precisely; it is the small deviations from this major behavior that perturbation theory will calculate. There are two types of problems for which we will develop approximation techniques; Time dependent and time independent Hamiltonian operators. We first consider time independent Hamiltonian operators. We will determine the approximate stationary states and energy eigenvalues for this case. Needless to say there are many approaches to this problem; we first consider the approach of Rayleigh and Schrödinger.

6.1. Rayleigh-Schrödinger Stationary State Perturbation Theory

Consider the case where the Hamiltonian is time independent. The Schrödinger equation becomes the energy eigenvalue equation for the stationary states $|\psi_n\rangle$

$$H|\psi_n\rangle = E_n|\psi_n\rangle,$$

where for convenience we label the energy eigenvalues with a discrete index n; they could in principle be continuous as well. Of course, these eigenvalues can be degenerate and we can include an additional label $k = 1, \ldots, g_n$ for the needed commuting operators A, $|\psi_{n,k}\rangle$.

In general we cannot solve this problem but must find approximate solutions to the stationary states. In particular, suppose

$$H = H_0 + H' = H_0 + \lambda\hat{H}', \quad \lambda \in \mathbb{R}.$$

where $|\lambda| << 1$ and $H_0, H', \hat{H}'$ are time independent and we can solve the unperturbed eigenvalue problem exactly. That is

$$H_0 |\varphi_{m,\ell}\rangle = E^0_m |\varphi_{m,\ell}\rangle$$

where E^0_m ($|\varphi_{m,\ell}\rangle$) are the known eigenvalues (eigenstates) of H_0. Again we label the energies E^0_m with a discrete index m; in general it could also be continuous. ℓ labels the possible unperturbed energy degenerate states. It could happen that the set of energies E_n, which are considered smooth functions of λ, have a different number of elements ~~than~~ the set E^0_m; i.e. 2 different $E_n(\lambda)$ approach the same E^0_m at $\lambda = 0$. As well, the degeneracies may be different i.e. $\ell \in 1, \dots, g^0_m$ while $k = 1, \dots, g_n$.

Further we assume that the states $|\varphi_{m,\ell}\rangle$ are orthonormal

$$\langle \varphi_{m',\ell'} | \varphi_{m,\ell}\rangle = \delta_{m'm}\delta_{\ell'\ell}$$

and complete $\mathbb{1} = \sum_m \sum_{\ell=0}^{g^0_m} |\varphi_{m,\ell}\rangle\langle\varphi_{m,\ell}|$.

The idea of the perturbation expansion is that when the perturbation is off, $\lambda = 0$, we have the energies E_m^0 and eigenstates $|\varphi_{m,\ell}\rangle$. Assuming the full energies and eigenstates vary smoothly with the perturbation strength λ, we determine, for a given initial energy E_m^0, the full energies E_n and states $|\psi_n\rangle$ as power series in λ.

Thus we assume that the energy eigensolutions to the full problem of

$$H|\psi_n\rangle = E_n|\psi_n\rangle$$

have Taylor series in the small (to be defined) perturbing interaction parameter λ:

$$E_n = \sum_{i=0}^{\infty} \lambda^i E_n^{(i)} = \underset{\substack{\parallel \\ E_n^0}}{\epsilon_n^{(0)}} + \lambda \epsilon_n^{(1)} + \lambda^2 \epsilon_n^{(2)} + \cdots$$

$$|\psi_n\rangle = \sum_{i=0}^{\infty} \lambda^i |\psi_n^{(i)}\rangle = |\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \cdots$$

with $E_n^{(i)}$ and $|\psi_n^{(i)}\rangle$ independent of λ.

Before determining the $E_n^{(i)}$ and $|\psi_n^{(i)}\rangle$ by using the Schrödinger equation, we consider the normalization constraints on $|\psi_n\rangle$. As we know, the Schrödinger equation determines $|\psi_n\rangle$ only up to an overall normalization constant (a complex number). We will fix the normalization by the following convention:

1) norm: $\langle\psi_n|\psi_n\rangle \equiv 1$

2) phase: $\langle\psi_n^{(0)}|\psi_n\rangle$ = Real number

These normalization conventions imply certain constraints on the $|\psi_n^{(i)}\rangle$:

$$1 = \langle\psi_n|\psi_n\rangle$$

$$= \left[\langle\psi_n^{(0)}| + \lambda\langle\psi_n^{(1)}| + \lambda^2\langle\psi_n^{(2)}| + \cdots\right] \times$$

$$\times \left[|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \cdots\right]$$

$$1 = \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle$$
$$+ \lambda \left[\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(0)} \rangle \right]$$
$$+ \lambda^2 \left\{ \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(2)} | \psi_n^{(0)} \rangle \right]$$
$$+ O(\lambda^3) .$$

Since λ is considered an independent parameter we set equal powers of λ equal to each other

$\Longrightarrow$

$$\boxed{\begin{aligned}
\lambda^0 &: \quad 1 = \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle \\
\lambda^1 &: \quad 0 = \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(0)} \rangle \\
\lambda^2 &: \quad 0 = \langle \psi_n^{(2)} | \psi_n^{(0)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle \\
&\vdots \\
\lambda^i &: \quad 0 = \langle \psi_n^{(i)} | \psi_n^{(0)} \rangle + \langle \psi_n^{(i-1)} | \psi_n^{(1)} \rangle \\
&\qquad + \cdots + \langle \psi_n^{(0)} | \psi_n^{(i)} \rangle \\
&\vdots
\end{aligned}}$$

From the phase normalization $\langle \psi_n^{(0)} | \psi_n \rangle$ = Real we find

$$\langle \psi_n^{(0)} | \psi_n \rangle = \langle \psi_n^{(0)} \Big| \Big(|\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \cdots \Big)$$

$$= \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle + \lambda \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + \lambda^2 \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle + \cdots$$

$\equiv$ real number.

Again equating equal powers of λ

λ^0 : $\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle$ = real (= 1 from above already)

λ^1 : $\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = \text{real} = \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle^*$

$$\Rightarrow \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = \langle \psi_n^{(1)} | \psi_n^{(0)} \rangle$$

λ^2 : $\langle \psi_n^{(0)} | \psi_n^{(2)} \rangle = \text{real} = \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle^*$

$$\Rightarrow \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle = \langle \psi_n^{(2)} | \psi_n^{(0)} \rangle$$

$\vdots$

$$\lambda^i : \langle \psi_n^{(0)} | \psi_n^{(i)} \rangle = \text{real} = \langle \psi_n^{(0)} | \psi_n^{(i)} \rangle^*$$

$$\Rightarrow \langle \psi_n^{(0)} | \psi_n^{(i)} \rangle = \langle \psi_n^{(i)} | \psi_n^{(0)} \rangle$$

$\vdots$

Combining this with the $\langle \psi_n | \psi_n \rangle = 1$ normalization implies

$$\lambda^0 : \quad 1 = \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle$$

$$\lambda^1 : \quad 0 = \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = \langle \psi_n^{(1)} | \psi_n^{(0)} \rangle$$

$$\lambda^2 : \quad 0 = 2\langle \psi_n^{(0)} | \psi_n^{(2)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle$$

$$\Rightarrow \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle = \langle \psi_n^{(2)} | \psi_n^{(0)} \rangle$$

$$= -\frac{1}{2} \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle$$

$\vdots$

$$\lambda^i : \langle \psi_n^{(0)} | \psi_n^{(i)} \rangle = \langle \psi_n^{(i)} | \psi_n^{(0)} \rangle$$

$$= -\frac{1}{2} \left[\langle \psi_n^{(i-1)} | \psi_n^{(1)} \rangle + \cdots + \langle \psi_n^{(1)} | \psi_n^{(i-1)} \rangle \right]$$

$\vdots$

We can next substitute the power series for H, E_n, $|\psi_n\rangle$ into the Schrödinger equation to determine the remaining energy coefficients and states.

$$H|\psi_n\rangle = E_n|\psi_n\rangle$$

becomes

$$(H_0+\lambda\hat{H}')\sum_{i=0}^{\infty}\lambda^i|\psi_n^{(i)}\rangle$$

$$=\left(\sum_{j=0}^{\infty}\lambda^j\epsilon_n^{(j)}\right)\left(\sum_{i=0}^{\infty}\lambda^i|\psi_n^{(i)}\rangle\right),$$

That is

$$(H_0+\lambda\hat{H}')\left(|\psi_n^{(0)}\rangle+\lambda|\psi_n^{(1)}\rangle+\lambda^2|\psi_n^{(2)}\rangle+\cdots\right)$$

$$=\left(\epsilon_n^{(0)}+\lambda\epsilon_n^{(1)}+\lambda^2\epsilon_n^{(2)}+\cdots\right)\times$$

$$\times\left(|\psi_n^{(0)}\rangle+\lambda|\psi_n^{(1)}\rangle+\cdots\right).$$

Once again equating the same powers of λ we find

λ^0: $\quad H_0 |\psi_n^{(0)}\rangle = \epsilon_n^{(0)} |\psi_n^{(0)}\rangle$

λ^1: $\quad H_0 |\psi_n^{(1)}\rangle + \hat{H}' |\psi_n^{(0)}\rangle = \epsilon_n^{(0)} |\psi_n^{(1)}\rangle + \epsilon_n^{(1)} |\psi_n^{(0)}\rangle$

$$\Rightarrow (H_0 - \epsilon_n^{(0)}) |\psi_n^{(1)}\rangle + (\hat{H}' - \epsilon_n^{(1)}) |\psi_n^{(0)}\rangle = 0$$

λ^2: $\quad H_0 |\psi_n^{(2)}\rangle + \hat{H}' |\psi_n^{(1)}\rangle = \epsilon_n^{(2)} |\psi_n^{(0)}\rangle + \epsilon_n^{(1)} |\psi_n^{(1)}\rangle + \epsilon_n^{(0)} |\psi_n\rangle$

$$\Rightarrow (H_0 - \epsilon_n^{(0)}) |\psi_n^{(2)}\rangle + (\hat{H}' - \epsilon_n^{(1)}) |\psi_n^{(1)}\rangle - \epsilon_n^{(2)} |\psi_n^{(0)}\rangle = 0$$

$\vdots$

λ^i: $\quad H_0 |\psi_n^{(i)}\rangle + \hat{H}' |\psi_n^{(i-1)}\rangle = \epsilon_n^{(i)} |\psi_n^{(0)}\rangle + \epsilon_n^{(1)} |\psi_n^{(i-1)}\rangle + \epsilon_n^{(i-1)} |\psi_n^{(1)}\rangle + \cdots + \epsilon_n^{(0)} |\psi_n^{(i)}\rangle$

$$\Rightarrow (H_0 - \epsilon_n^{(0)}) |\psi_n^{(i)}\rangle + (\hat{H}' - \epsilon_n^{(1)}) |\psi_n^{(i-1)}\rangle - \epsilon_n^{(2)} |\psi_n^{(i-2)}\rangle - \cdots - \epsilon_n^{(i)} |\psi_n^{(0)}\rangle = 0$$

$\vdots$

The λ^0 term $\Rightarrow$

$$H_0 |\psi_n^{(0)}\rangle = \epsilon_n^{(0)} |\psi_n^{(0)}\rangle .$$

Thus $|\psi_n^{(0)}\rangle$ is an eigenvector of H_0 with eigenvalue $\epsilon_n^{(0)}$. Thus $\epsilon_n^{(0)}$ belongs to the spectrum of H_0. This is expected since we assumed that each eigenvalue of H approached, as $\lambda \to 0$, one of the eigenvalues of $H\big|_{\lambda=0} = H_0$, an unperturbed energy.

So we choose a particular value for $\epsilon_n^{(0)}$; say $\epsilon_n^{(0)} = E_n^0$.

It could be that several energies $E = E(\lambda)$ approach E_n^0 as $\lambda \to 0$, the eigenstates of these $E(\lambda) \xrightarrow[\lambda \to 0]{} E_n^0$ span a vector subspace whose dimension is the degeneracy of E_n^0, g_n. If E_n^0 is non-degenerate, it can evolve only into one $E(\lambda)$ and this energy is non-degenerate.

For simplicity we consider first the case where $\underline{E_n^0}$ is <u>non-degenerate</u>