Understanding Accidental Degeneracies of Hydrogen

\[ [L_z, H] = 0, \quad [L^2, H] = 0 \]
so \( \{n, l, m\} \) states are degenerate. Form vector

\[
\vec{N} = \frac{1}{2m} \left( \vec{r} \times \vec{p} - \vec{p} \times \vec{r} \right) - \frac{e^2 \vec{R}}{(x^2 + y^2 + z^2)^{3/2}}
\]

\[ [N_z, H] = 0 \]

Ni relates electron. Form the components that are spherical

\[
N^\pm_1 = \frac{1}{\sqrt{2}} \left( N_x \pm i N_y \right)
\]

Now consider state \( |n, l, e\rangle \). Action \( A \) with \( N^\pm_1 \) produces state with same energy, degenerate but

\[ \text{s} \]

Hydrogen angular mom \( \frac{1}{\sqrt{2}} (N_x \pm i N_y) \)

\[
\text{So states with different \( l \) 's degenerate. Find energy level:}
\]

\[
\Delta = \text{max} \] 

\[ \text{The Variation Method} \]

Let \( E_0 \) be ground state (lowest energy eigenvalue)

of Hamiltonian

\[
E \left[ \Psi \right] = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} > E_0
\]

Grand state \( |\Psi\rangle \) is a superposition of energy states

\[
|\Psi\rangle = \sum_n a_n |E_n\rangle
\]
Suggest a method of determining ground state energy.

Take all states in Hilbert space forming them one by one and one will obtain $E(L_4)$. Not practical. Usually used to get an approximate ground state energy by choosing basis on some subset of Hilbert space parametrized by some number ($\{\phi_1, \phi_2, \ldots\}$) Calculate $E(L_4)$ for each minimizer $E(\phi_1, \phi_2, \ldots)$ provide an upper bound on $E_0$.

Eg. 1-dim particle in mass $M$ moving in pot $V(x) = \lambda x^4$.

Ground state cut off well for no quas free particle cloud $x = 0$ with $\phi(x) \rightarrow 0$. Trial cut

$$\Psi(x) = e^{-\frac{ax^2}{2}}$$

where $a$ is the parameter.

$$\langle \Psi | \Psi \rangle = \int_{-\infty}^{\infty} dx \ e^{-\frac{ax^2}{2}} = \frac{1}{\sqrt{\pi a}} \int_{-\infty}^{\infty} dy \ e^{-\frac{y^2}{a}} = \sqrt{\frac{\pi}{a}}$$

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \lambda x^4$$

$$\langle \Psi | H | \Psi \rangle = \int_{-\infty}^{\infty} dx \left[ \frac{\hbar^2}{2m} \cdot 2xe^{-\frac{ax^2}{2}} \right] + \lambda x^4 e^{-\frac{ax^2}{2}}$$
\[ \begin{align*}
= & \frac{-\hbar^2}{2m} \int_{-\infty}^{\infty} y^2 e^{-y^2} dy + \frac{1}{\alpha x} \int_{-\infty}^{\infty} y e^{-y^2} dy \\
= & \frac{\alpha^2 \hbar^2}{2m} \frac{1}{\alpha x^2} + \frac{1}{\alpha x} \left( \frac{3\sqrt{\pi}}{4} \right)
\end{align*} \]

\[ E(X) = \frac{\alpha^2 X}{2m} + \frac{3\lambda}{4X^2} \]

Best check out

\[ \frac{dE}{d\alpha} = 0 \quad \frac{\Delta^2}{4m} + \frac{3\lambda}{4\alpha^2} = 0 \]

\[ \alpha = \left( \frac{6m \lambda}{\hbar^2} \right)^{\frac{1}{3}} \]

And our best guess for the energy is

\[ E(\alpha) = \frac{\alpha^2}{4m} \left( \frac{6m \lambda}{\hbar^2} \right)^{\frac{1}{3}} + \frac{3\lambda}{4} \left( \frac{\alpha^2}{6m \lambda} \right)^{\frac{2}{3}} \]

\[ = \left( \frac{6\hbar^4 \lambda}{m^2} \right)^{\frac{1}{3}} \left( \frac{\alpha}{\sqrt{4 \lambda}} \right) \left( \frac{3}{\sqrt{8}} \right) \]

Let's see a case where we actually know the ground state.

**Eg. Ground state of Hydrogen**

\[ V = -\frac{e^2}{r} \quad \text{To} \quad \psi(r, \theta, \phi) = e^{-\lambda r} \]

\[ H = \frac{-\hbar^2}{2m} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{e^2}{r} \]
\[\int_0^\infty \frac{e^{-ax^2}}{r^2} \, dr = -\frac{1}{a} \int_0^\infty \left( \frac{d}{dr} \left( r^2 e^{-ax^2} \right) \right) \left( \frac{d}{dr} e^{-ax^2} \right) \, dr\]

\[= -\frac{4}{a} \int_0^\infty d^2 r \, e^{-2ax^2} \]

\[= -\frac{4}{a} \int_0^\infty x^2 y^2 e^{-2y^2} \, dy \]

\[= \left( -\frac{4}{a} \right) \left( \frac{\pi^{\frac{3}{2}}}{8} \right) \]

\[\int_0^\infty r^2 e^{-2ax^2} \, dr = \left( \frac{1}{a} \right)^3 \int_0^\infty y^2 e^{-2y^2} \, dy \]

\[= \left( \frac{1}{a} \right)^3 \left( \frac{\pi^{\frac{3}{2}}}{8} \right) \]

\[\int_0^\infty \frac{1}{r^2} e^{-2ax^2} \, dr = \int_0^\infty e^{-2ax^2} \, dr \]

\[= \frac{1}{ax} \int_0^\infty e^{-2y^2} \, dy \]

\[= \frac{1}{ax} \]
So pull this together

$$E(x) = \left( \frac{1}{\sqrt{2} \pi} \right)^{3/2} \frac{e^{-x^2}}{\sqrt{2 \pi}} \left[ -\frac{\hbar^2}{2m} \frac{3}{8} \left( \frac{\hbar}{\sqrt{2}} \right)^2 \frac{\sqrt{\pi}}{2} \right] \left( -\frac{e^2}{r} \right) \left( \frac{1}{4\pi} \right)$$

$$= \frac{3\hbar^2}{2m} x - \left( \frac{2}{\pi} \right)^{1/2} 2e^2 \sqrt{x}$$

$$\frac{dE}{dx} = 0 \rightarrow \frac{3\hbar^2}{2m} - \frac{2}{\pi} \frac{e^2}{\sqrt{x}} = 0$$

$$x_0 = \left( \frac{me^2}{\hbar^2} \right)^2 \frac{8}{9\pi}$$

$$E(x_0) = -\frac{me^4}{2\hbar^2} \frac{8}{5\pi} = -0.85 \frac{e^2}{\hbar^2}$$

$$L_y = \left( \frac{me^2}{2\hbar^2} \right)$$

Eq. Ground State Helium

$$H = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) - \frac{2e^2}{\sqrt{\alpha_1}} - \frac{2e^2}{\sqrt{\alpha_2}} + \frac{e^2}{\alpha_2}$$

$$\alpha_1, \alpha_2$$ are core radial coordinates and $$\alpha_2$$ is radial size below then.
We have already studied a mutual potential $e^2/4\pi\epsilon_0$ in ground state at:

$$\Psi = \Psi_{100}(r_1) \Psi_{100}(r_2)$$

This is ground state of hydrogen with $Z = 1$.

$$\Psi_{100} = \left( \frac{Z^3}{\pi \alpha^3} \right)^{1/2} e^{-Z/r_0} \quad Z = Z$$

$$\Psi = \left( \frac{Z^3}{\pi \alpha^3} \right)^{1/2} e^{-Z(r_1 + r_2)/\alpha_0}$$

But this relation holds valid when

$$E = \frac{2}{x^2} \left( -\frac{m(2e^2)^2}{2\alpha^2} \right) = -108.8 \text{ eV}$$

True ground state energy is $-78.6 \text{ eV}$. Not controllable at all, not very good. Suppose you try this as a limit, but need $Z$ as a variational constant. Final menu at not $Z = 0$ and

$$Z_0 = 27/16 = 2 - 5/16$$

$$E = 77.5 \text{ eV}$$

actually very good guess.

One aspect of the variational approach still makes it work better than one might naively think is the Hubbar - $S$ eigen at variational level:

$$147 = 1E_0 + \left( \frac{4}{10} \right) 1E_1$$

So 10% contamination on the state $1E_1$. Estimate energy
\[ E(\psi) = \frac{\langle B_0 | H | B_0 \rangle + \frac{1}{100} \langle E_1 | H | E_1 \rangle}{1 + \frac{1}{100}} \]

\[ \approx 0.99 E_0 + 0.01 E_1 \]

what will be, only \( \approx 1\% \) if \( E_1 \) is not much large than \( E_0 \). More generally if

\[ |\Psi_1\rangle = |B_0\rangle + i|\delta\rangle \]

We may express \( |\delta\rangle \) into a product \( |B_0\rangle \) of a grand algebra

\[ |\delta\rangle = |\delta_{1}\rangle_{\downarrow} + |\delta_{1}\rangle_{\uparrow} \]

\[ = |B_0\rangle + i|\delta\rangle \]

\[ \langle E_0 | \delta \delta \rangle = 0 \]

\[ EL\psi = E_0 |1 + k_1^2 + \langle \delta \delta | H | \delta \delta \rangle \]

\[ \frac{1}{1 + k_1^2 + \langle \delta \delta | H | \delta \delta \rangle} \]

\[ = E_0 + O(k_1^2) \]

All these are true for any spin \( S \) of \( \mathbf{S} \) of \( 1 \mathbf{e}_{z} \approx 1 E_{n} + |\delta_{n}\rangle \)

\( \delta_{n} \) approx to \( E_{n} \) then

\[ EL\psi = E_{n} + O(\delta_{n}^2) \]

We expect that we changed it but only the energy will change of second order.
The WKB Method

Consider a particle of energy $E$ moving in a constant potential $V$. Energy eigenfunctions are (1-4.3m)

$$\psi(x) = \psi(0) e^{i \frac{2\pi}{\hbar} x}$$

$$\rho = \left[ \frac{2m(E-V)}{\hbar^2} \right]^{1/2}$$

$m$ is wavelength which corresponds to right and left moves over length $\lambda$. i.e. of time $\rho$. Real $\rho$ imagiary part oscillates well across $x$

$$\lambda = \frac{2\pi \hbar}{P}$$

Now suppose instead of being constant $V(x)$ varies very slowly. Then over some region $\Gamma$ should still behave like a plane wave but with a spatially dependent wavelength

$$\lambda(x) = \frac{2\pi \hbar}{P(x)} = \frac{2\pi \hbar}{\sqrt{2m[E-V(x)]}}$$

Define $\frac{\partial}{\partial x}$

$$\psi(x) = \psi(0) e^{i \int \frac{\rho \, dx}{\hbar}}$$

More generally

$$\psi(x) = \psi(0) e^{i \int \frac{\rho(x') \, dx'}{\hbar}}$$

How slow is slow enough to take to be

$$\left| \frac{\partial}{\partial x} \right| < C$$

$$\left| \frac{\partial}{\partial x} \frac{\rho(x) \, dx}{\hbar} \right| < C \Rightarrow \frac{\rho}{\hbar} = \frac{\rho(x)}{\hbar}$$
Well this is no dermal just induction lets go a
real derivation

We are trying to solve

$$\left\{ \frac{d^2}{dx^2} + \frac{2m}{\hbar^2} \left[ E - V(x) \right] \right\} \psi(x) = 0$$

$$\left\{ \frac{d^5}{dx^5} + \frac{1}{\hbar^2} \psi''(x) \right\} \psi(x) = 0$$

While

$$\psi(x) = \exp \left[ \frac{i \phi(x)}{\hbar} \right]$$

$\phi(x)$ not assumed to be real.

$$\frac{d\psi}{dx} = \frac{i \phi(x)}{\hbar} e^{\frac{i \phi(x)}{\hbar}}$$

$$\frac{d^3\psi}{dx^3} = \left[ -\frac{i \phi''(x)}{\hbar} - \frac{(\phi(x))^2}{\hbar^2} \right] e^{\frac{i \phi(x)}{\hbar}}$$

$$-\left( \phi' \right)^2_{\frac{i}{\hbar}} + \frac{i \phi'' + \phi(x)^2}{\hbar^2} = 0$$

Now expand $\phi(x)$ in a power series in $\hbar$

$$\phi(x) = \phi_0 + \hbar \phi_1 + \hbar^2 \phi_2 + \ldots$$

In $1\text{m} \cdot \hbar = 0$ units $\lambda = \frac{2\pi \hbar}{\mu} = 0$ so
potential can be treated as constant or many wavelengths?
WKB approximation simply that claims above
\[- \left( \frac{\phi'_0}{x} \right)^2 + \rho(x) \phi'_0^2 + i \phi''_0 - 2 \phi'_0 \phi_0 + \theta \phi_0^2 = 0 \]

\[\phi'_0 = \pm \rho(x)\]

\[\phi_0(x) = \pm \int^x \rho(x') dx'\]

Keying the term

\[\Psi(x) = \Psi(x_0) \exp \left[ \pm \left( \frac{i}{\hbar} \right) \int^x \rho(x') dx' \right]\]

Now we shall get \(\phi_1\)

\[i \phi''_0 = 2 \phi'_0 \phi'_0\]

\[\phi''_0 = -2i \phi'_0\]

\[\kappa (\phi'_0) = -2i \phi'_0 + c\]

\[\phi_1 = i \ln \left( \phi'_0 \right)^{1/2} + \frac{c}{2\hbar}\]

\[= i \kappa p^{1/2} + \xi\]

\[\Psi(x) = A e^{-i \ln \left( \rho(x) \right)^{1/2}} \exp \left[ \pm \left( \frac{i}{\hbar} \right) \int^x \rho(x') dx' \right]\]

\[= \frac{A}{\sqrt{\rho(x)}} \exp \left[ \pm \left( \frac{i}{\hbar} \right) \int^x \rho(x) dx' \right]\]
\[ \Psi(x) = \Psi(x_0) \left( \frac{p(x_0)}{p(x)} \right)^{1/2} \exp \left[ \pm \frac{i}{\hbar} \int_{x_0}^{x} p(x') dx' \right] \]

\[ g(x) = |\Psi(x)|^2 \propto \frac{1}{p(x)} \]

Need \( \phi_c \) for to be equal to \( \phi_0 \) in the\*