Ph125b Lecture Notes

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Contents

Results

1: Logistics

1.1. Overview

- Sets are turned into Gradescope
- Post questions on Piazza

1.2. Notation

- The symbol $\mid$ is "such that", such as $x \mid x \geq n$ and $x \in \mathbb{N}$ is "x such that $x \geq n$ and x is a natural number."
- $\mathbb{N}$ are non-negative integers, $\mathbb{N}_+$ is strictly positive integers.
- Similarly for $\mathbb{R}, \mathbb{R}_+$, and $\mathbb{R}_-$.
- Matrices, operators, and higher order tensors will normally be hatted, capitalized, and uprighted, such as $\hat{\mathrm{H}}, \hat{\mathbf{X}}, \hat{\mathbf{S}}, \hat{\mathrm{V}}, \hat{\mathrm{C}}$, etc. When such symbols are boldened, this denotes a vector operator/tensor, with a natural action on some space.
- The symbol $:=$ is an explicit definition. I.e. $f(x) := \sin(x)^2$ implies that we have not yet "seen" $f(x)$ used. If $n := n + 1$ or $n \mapsto n + 1$ (where $\mapsto$ is a mapping like in mathematics) is written, then we "forget" the prveious value of n.
- τ may denote the alternative circle constant, the ratio of the circumference to the radius. Most cases it will be clear what we're talking about, especially since I rarely use τ for other things, if not just use some common sense.
- $\left[f(x)\right|_{x=x_0}^{x=x_1}$ means $f(x_1) - f(x_0)$. Sometimes the superscript and subscript will be modified if it's clear from context, e.g. $\left[\psi(t)\right|_T = \psi(T)$.

1.3. Notes for the Reader

I've done my best to ensure there's no typos, but undoubtably there shall be some. In particular, I've noticed that when reading 3's on the lecture board, they're often wrongly transcripted to 2's. This is especially true for exponents.

If the reader finds any typo, you are welcome to email me or contact me anyway you find fit.

The source code for this is freely available, but is currently not hosted anywhere, so if you'd like the source code, again email with the link above. The code is however not written in LaTeX, but rather in Typst. If you haven't tried it, I very much recommend it.

1.4. Notes for the Author & Reading the Original Work

- Typesetter Notation: Underlining is typesetting for bold, so $\underline{x} = \boldsymbol{x} = \vec{x}$

2: WKB Method

2.1. The Idea

The goal of the Wentzel-Krumers-Brillouin Method is to estimate the spectrum of a Hamiltonian by making use of the wave-nature of the Schrödinger Equation in correspodnence to the classical turning points. We begin by labelling the energy eigenstates $|n\rangle$ with energy E_n

2.2. Formulation

Consider now E_n with classical turning points (x_1, x_2) within a single interval (that is points where we have $\hat{\mathrm{V}}(x) = E_n$. We know that E_n corresponds to the $(n+1)$-th state, or the n-th excited state. Between the classical turning points, the wavefunction will be primarily oscillatory in nature, as can be seen by the Schrödinger Equation. In particular, there will be roughly $n+1$ half-waves between the two turning points. Stating this more formally, let $\Delta\varphi_n$ be the total phase change of the the wave function between the turning points for $|n\rangle$. We have:

$$\Delta\varphi_n \approx \left(n + \frac{1}{2}\right)\pi \tag{1}$$

or more rigorously,

$$n\pi < \Delta\varphi_n \leq (n+1)\pi \tag{2}$$

where equality would occur if, for example, we had an infinite square well potential. Here, we'll just assume the previous approximate value.

Now recognize that for a region of constant $\hat{\mathrm{V}} < E_n$, we must have:

$$\psi(x) = A \sin P(x - x_0) \tag{3}$$

where A, x_0 are constants and

$$P = \sqrt{2m(E-V)} \tag{4}$$

Without loss of generality,

$$\varphi(x) = p(x - x_0) \tag{5}$$

in the region of constant $\hat{\mathrm{V}}$. But we may generalize this for non-constant $\hat{\mathrm{V}}$ with:

$$\mathrm{d}\varphi(x) = p\mathrm{d}x = \sqrt{2m(E-V)}\mathrm{d}x \tag{6}$$

And we find that we must have:

$$\Delta\varphi = \int_{x_1}^{x_2} \frac{\mathrm{d}\varphi}{\mathrm{d}x}\mathrm{d}x = \int_{x_1}^{x_2} \sqrt{2m(E-V)}\mathrm{d}x \tag{7}$$

but from the previous approximation, we must have:

$$\left(n + \frac{1}{2}\right)\pi \approx \int_{x_1}^{x_2} \sqrt{2m(E-V)}\mathrm{d}x \tag{8}$$

This gives us a reasonable approximation for the energy levels for any given potential (which also provides x_1, x_2).

2.3. Examples

Example 2.3:1 (Infinite Square Well)

We have:

$$x_1 = 0 \quad ; \quad x_2 = \Delta \quad ; \quad \hat{\mathrm{V}} = 0 \tag{9}$$

Therefore:

$$\int_0^{\Delta} \sqrt{2mE}\mathrm{d}x = \sqrt{2mE}\Delta \tag{10}$$

$$\sqrt{2mE}\Delta \approx \left(n + \frac{1}{2}\right)\pi \tag{11}$$

$$E_n = \frac{\left(n + \frac{1}{2}\right)^2 \pi^2}{2m\Delta^2} \tag{12}$$

Giving the exact answer. We could have also solved this from the fact that the boundary conditions inherently specify the exact change in phase.

Example 2.3:2 (1D Harmonic Oscillator)

We again have:

$$x_1 = -x_2 = \sqrt{2\frac{E}{k}} \quad ; \quad \hat{\mathrm{V}}(x) = \frac{1}{2}kx^2 \tag{13}$$

Now:

$$2\sqrt{mk}\int_0^{x_0} \sqrt{x_0^2 - x^2}\mathrm{d}x \tag{14}$$

$$= \frac{\pi x_0^2}{2}\sqrt{mk} = \pi\frac{E}{\omega_0} \quad ; \quad \omega_0 = \sqrt{\frac{k}{m}} \tag{15}$$

$$\approx \left(n + \frac{1}{2}\right)\pi \Rightarrow E_n = \left(n + \frac{1}{2}\right)\omega_0 \tag{16}$$

which is once again an exact result.

3: Variational Method

3.1. The Idea

Recall that, for any wave function ψ and any Hamiltonian, we must have:

Theorem 3.1:1 (Energy Lower Bound)

$$\frac{\langle\psi|\hat{\mathrm{H}}|\psi\rangle}{\langle\psi\,|\,\psi\rangle} \geq E_0 \tag{1}$$

Thus one approach to calculate E_0 is by calculating this for some ψ, or in today's approach, some family of ψ's. In particular, let's resort to a variational method to determine the ground energy. The process is as follows:

- Make an educated guess for a solution to the Schrödinger Equation.
- Parameterize it.
- Use variational calculus to minimize $\langle\psi|\hat{\mathrm{H}}|\psi\rangle$.
- Obtain an upper bound on the ground state energy.

Let E_0 be the ground state energy. Note that for any wavefunction $\psi \in \mathcal{H}$, that we must have:

$$\frac{\langle\psi|\hat{\mathrm{H}}|\psi\rangle}{\langle\psi\,|\,\psi\rangle} \geq E_0 \tag{2}$$

This suggests using some set of ψ parameterized by some variable, call it α. We can then vary α and minimize the quantity above using variational calculus:

$$\frac{\delta\left\{\frac{\langle\psi(\alpha)|\hat{\mathrm{H}}|\psi(\alpha)\rangle}{\langle\psi(\alpha)\,|\,\psi(\alpha)\rangle}\right\}}{\delta\{\alpha\}} = 0 \tag{3}$$

3.2. Examples

Example 3.2:1 (The Helium Atom)

Let $\boldsymbol{R} = \boldsymbol{r}_1 - \boldsymbol{r}_2$

$$\hat{\mathrm{H}} = \frac{\hat{\mathbf{P}}_1^2}{2m} + \frac{\hat{\mathbf{P}}_1^2}{2m} - \frac{2\alpha}{|\boldsymbol{r}_1|} - \frac{2\alpha}{|\boldsymbol{r}_2|} + \frac{\alpha}{|\boldsymbol{R}|} \tag{4}$$

Where $m = m_e$ and neglecting the motion of the nucleus. Note that we've already solved this without the last term, this is just twice the hydrogen atom otherwise.

We guess:

$$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{Z^3}{\pi} a_0^3 \exp\left(-\frac{Z}{a_0}(\boldsymbol{r}_1 + \boldsymbol{r}_2)\right) \tag{5}$$

Where

$$Z = 2 \quad ; \quad a_0 = \frac{1}{m\alpha} \tag{6}$$

Remark 3.2:2

Note there is no reason to expect that the interaction term to be "small." It is roughly of the same order as the two other Coulomb potentials in the Hamiltonian. When we get to pertubation theory, we'll see **Example 4.3.1** where we'll instead add "small" corrections, but examples like these are where the variational method shines.

We will be choosing Z as our variational parameter. We note that $\psi(Z)$ is already normalized. We start by taking the expectation value of H:

$$\left\langle \psi \left| \frac{\hat{\mathbf{P}}_1^2}{2m} \right| \psi \right\rangle = \int \mathrm{d}^3(\boldsymbol{x}_1) \left(\frac{Z^3}{\pi a_0^3} e^{-\frac{Z}{a_0}\boldsymbol{r}_1} \right) \frac{\hat{\mathbf{P}}_1^2}{2m} \left(\frac{Z^3}{\pi a_0^3} e^{-\frac{Z}{a_0}\boldsymbol{r}_1} \right) \tag{7}$$

$$= Z^2 \times (\text{K.E. of the H atom ground state.}) \tag{8}$$

$$= \frac{Z^2}{2} m\alpha^2 \tag{9}$$

$$\Rightarrow \left\langle \psi \left| \frac{\hat{\mathbf{P}}_1^2 + \hat{\mathbf{P}}_2^2}{2m} \right| \psi \right\rangle = Z^2 m\alpha^2 \tag{10}$$

Likewise we can do something similar for the Coulomb term:

$$\left\langle \psi \left| -2\frac{\alpha}{\boldsymbol{r}_1} \right| \psi \right\rangle = 2Z(\text{P.E. of the H atom ground state.}) \tag{11}$$

$$= -2Zm\alpha^2 = -2\alpha\langle \frac{1}{\boldsymbol{r}_1} \rangle \tag{12}$$

So far we have:

$$\Rightarrow \left\langle \psi \left| \frac{\hat{\mathbf{P}}_1^2 + \hat{\mathbf{P}}_2^2}{2m} - 2\alpha\left(\frac{1}{\boldsymbol{r}_1} + \frac{1}{\boldsymbol{r}_2} \right) \right| \psi \right\rangle = \frac{1}{2} m\alpha(2Z^2 - 8Z) \tag{13}$$

Now we just need the last piece:

$$\left\langle \psi \left| \frac{\alpha}{\boldsymbol{R}} \right| \psi \right\rangle = \alpha \iint \mathrm{d}^2(\boldsymbol{r}_1)\mathrm{d}^3(\boldsymbol{r}_2) \tag{3.2:14}$$

Let's now take a moment to digress to some handy integrals we'll need in the future:

Theorem 3.2:3 (Integration Theorem I)

If $u > 0$ and $v > 0$ (one of which may be 0 but not both).

$$I(u, v; \boldsymbol{x}', \boldsymbol{x}'') := \int \mathrm{d}^3(\boldsymbol{y}) \frac{\exp(-u\,|\,\boldsymbol{y} - \boldsymbol{x}'\,| - v\,|\,\boldsymbol{y} - \boldsymbol{x}''\,)}{|\boldsymbol{y} - \boldsymbol{x}'|\;|\boldsymbol{y} - \boldsymbol{x}''|} \tag{15}$$

$$= \frac{4\pi\left(e^{-v\Delta} - e^{-u\Delta}\right)}{\Delta(u^2 - v^2)} \tag{16}$$

Where

$$\Delta = |\boldsymbol{x}' - \boldsymbol{x}''| \tag{17}$$

Theorem 3.2:4 (Integration Theorem II)

If $u > 0, v > 0, w > 0$ (only one of which may be 0), then

$$J(u,v,w) := \int \mathrm{d}^3(\boldsymbol{x})\mathrm{d}^3(\boldsymbol{y}) \frac{\exp(-u\,|\,\boldsymbol{x}\,| - v\,|\,\boldsymbol{y}\,| - w\,|\,\boldsymbol{x}-\boldsymbol{y}\,|)}{|\boldsymbol{x}|\;|\boldsymbol{y}|\;|\boldsymbol{x}-\boldsymbol{y}|} \tag{18}$$

$$= \frac{(4\pi)^2}{(u+v)(v+w)(w+u)} \tag{19}$$

Sketch of *Integration Theorems I & II* (3.2:5):

- Let $\boldsymbol{z} = \boldsymbol{y} - \boldsymbol{x}$ and $|\boldsymbol{z}| = r$.
- Move to $\mathrm{d}^3(\boldsymbol{z})$
- Apply spherical coordinates to the integral.
- Pick 3-axis along $\boldsymbol{x} - \boldsymbol{y}$ direction.
- Integrate over the angles.
- Apply trig identity (?).
- Integrate over radius.

■

With this, we're now just within reach of solving for **Equation (14)**:

$$\left\langle \psi \left| \frac{\alpha}{\boldsymbol{R}} \right| \psi \right\rangle = \alpha \iint_\infty \mathrm{d}^3(\boldsymbol{x}_1)\mathrm{d}^3(\boldsymbol{x}_2) \left(\frac{Z^3}{\pi a_0^2}\right)^2 \frac{\exp\left(-\frac{2Z}{a_0}\right)(\boldsymbol{r}_1 + \boldsymbol{r}_2)}{\|\boldsymbol{x}_1 - \boldsymbol{x}_2\|} \tag{20}$$

$$= \alpha \left(\frac{Z^3}{\pi a_0^2}\right)^2 \iint_\infty \mathrm{d}^3(\boldsymbol{x})\mathrm{d}^3(\boldsymbol{y}) \frac{\exp\left(-2\frac{Z}{a_0}(\boldsymbol{x}+\boldsymbol{y})\right)}{\|\boldsymbol{x}-\boldsymbol{y}\|} \tag{21}$$

Now we can put this in the following form:

$$J(u,v,w) := \int_\infty \mathrm{d}^3(\boldsymbol{x}) \int_\infty \mathrm{d}^3(\boldsymbol{y}) \frac{\exp(-u\|\boldsymbol{x}\| - v\|\boldsymbol{y}\| - w\|\boldsymbol{x}-\boldsymbol{y}\|)}{\|\boldsymbol{x}\|\|\boldsymbol{y}\|\|\boldsymbol{x}-\boldsymbol{y}\|} \tag{22}$$

Where this is now integrable by **Theorem 3.2.4**. We obtain:

$$= \alpha \left(\frac{Z^3}{\pi a_0^2}\right)^2 \partial_u \partial_v J(u,v,0) \tag{23}$$

$$= \frac{1}{2} m\alpha^2 \frac{5}{4} Z \tag{24}$$

$$\langle \psi | \hat{\mathrm{H}} | \psi \rangle = \frac{1}{2} m\alpha^2 \left(2z^2 - 8z + \frac{5}{4}\boldsymbol{z}\right) = \frac{1}{2} m\alpha^2 \left(2z^2 - \frac{27}{4} z\right) \tag{25}$$

Minimality implies

$$0 = 4Z - \frac{27}{4} \Rightarrow z = \frac{27}{16} \tag{26}$$

$$-\frac{1}{2} m\alpha^2 \left(2\left(\frac{27}{16}\right)^2\right) \approx -77.0\ eV \tag{27}$$

Experiment gives:

$$-78.60\ eV, \quad +2\%\ \text{of our guess.} \tag{28}$$

The fact that the minimum value for $Z = \frac{27}{16}$ also tells us something else heuristically. That the "effective charge" of the nucleus is reduced by the screening of the electrons.

3.3. Variational Theorem

Theorem 3.3:1 (Variational Theorem)

Let $\psi \in \mathcal{H} \mid 0 < \langle\psi \,|\, \psi\rangle < \infty$. Definite the functional:

$$E[\psi] := \frac{\langle\psi|\hat{\mathrm{H}}|\psi\rangle}{\langle\psi \,|\, \psi\rangle} \tag{29}$$

and $\hat{\mathrm{H}}$ a linear operator with a discrete spectrum. Then any $\psi \mid$ variation is stationary, that is, $\delta(E[\psi]) = 0$ is an eigenvector of $\hat{\mathrm{H}}$ with eigenvalue $E(\psi)$ and vice-versa.

Proof (3.3:2):

$$E[\psi]\langle\psi \,|\, \psi\rangle = \langle\psi|\hat{\mathrm{H}}|\psi\rangle \tag{30}$$

$$\delta(E[\psi]\langle\psi \,|\, \psi\rangle) = \delta\langle\psi|\hat{\mathrm{H}}|\psi\rangle \tag{31}$$

$$(\delta E[\psi])\langle\psi \,|\, \psi\rangle + E[\psi]\langle\delta\psi \,|\, \psi\rangle + E[\psi]\langle\psi \,|\, \delta\psi\rangle = \left\langle\delta\psi\,\middle|\,\hat{\mathrm{H}}\,\middle|\,\psi\right\rangle + \left\langle\psi\,\middle|\,\hat{\mathrm{H}}\,\middle|\,\delta\psi\right\rangle \tag{32}$$

Where $\delta\hat{\mathrm{H}} = 0$ since it's an operator independent of our parameter.

$$\delta E[\psi]\langle\psi \,|\, \psi\rangle = \left\langle\delta\psi\,\middle|\,\hat{\mathrm{H}} - E\,\middle|\,\psi\right\rangle + \left\langle\psi\,\middle|\,\hat{\mathrm{H}} - E\,\middle|\,\delta\psi\right\rangle \tag{33}$$

If $\left(\hat{\mathrm{H}} - E\right)|\psi\rangle = 0$, then $\delta E = 0$, i.e. if ψ is an eigenstate then it is then the $E[\psi]$ is stationary.

Suppose now that $\delta E = 0$. Then:

$$\left\langle\delta\psi\,\middle|\,\hat{\mathrm{H}} - E\,\middle|\,\psi\right\rangle + \left\langle\psi\,\middle|\,\hat{\mathrm{H}} - E\,\middle|\,\delta\psi\right\rangle = 0 \tag{3.3:34}$$

But ψ is complex. And so in particular variation is independent over both the real parts and the imaginary parts. And if $\delta E = 0$,

$$\left\langle\delta(i\psi)\,\middle|\,\hat{\mathrm{H}} - E\,\middle|\,\psi\right\rangle + \left\langle\psi\,\middle|\,\hat{\mathrm{H}} - E\,\middle|\,\delta(i\psi)\right\rangle = 0 \tag{35}$$

$$-i\left\langle\delta\psi\,\middle|\,\hat{\mathrm{H}} - E\,\middle|\,\psi\right\rangle + i\left\langle\psi\,\middle|\,\hat{\mathrm{H}} - E\,\middle|\,\delta\psi\right\rangle = 0 \tag{36}$$

Adding the previous equation,

$$\left\langle\delta\psi\,\middle|\,\hat{\mathrm{H}} - E\,\middle|\,\psi\right\rangle = 0, \forall\delta\psi \tag{37}$$

$$\Rightarrow \hat{\mathrm{H}}|\psi\rangle = E|\psi\rangle \tag{38}$$

■

3.4. Rayleigh-Ritz Variational Method

Imagine choosing a set of trial, orthonormal wave functions. With the helium method, we chose parameterized wave functions. Now, we'll take this independent set and form linear combinations of them. Let us label them $|n\rangle$ for $n \in \mathbb{N} \leq N$.

$$|\psi\rangle = \sum_n a_n |n\rangle \tag{39}$$

The a_n are $N+1$ complex parameters to be varied. Requiring $\langle\psi,\psi\rangle = 1$ we constrain

$$\sum_n \|a_n\|^2 = 1 \tag{40}$$

We want to find $\{a_n\}$ such that $\delta\left\langle \psi \middle| \hat{\mathrm{H}} \middle| \psi \right\rangle = 0$. Then

$$0 = \delta\left(\sum_{m,n} \langle\psi \,|\, m\rangle \left\langle m \middle| \hat{\mathrm{H}} \middle| n \right\rangle \langle n \,|\, \psi\rangle\right) \tag{41}$$

subject to

$$0 = \delta(1) = \delta\left(\sum_n \|a_n\|^2\right) = \delta\left(\sum_{m,n} a_m^* a_n \delta_{m,n}\right) \tag{42}$$

Which we include with the Lagrange multiplier:

$$\delta\left(\sum_{m,n} a_m^* a_n \left\langle m \middle| \hat{\mathrm{H}} \middle| n \right\rangle\right) = \delta\left(\lambda \sum_{m,n} a_m^* a_n \delta_{m,n}\right) \tag{43}$$

$$0 = \sum_{m,n} (\delta a_m^* a_n \left(\left\langle m \middle| \hat{\mathrm{H}} \middle| n \right\rangle\right) - \lambda\delta_{m,n} + a_m^*(\delta a_n)(\langle m \,|\, H \,|\, n\rangle) - \lambda\delta_{m,n} \tag{44}$$

$$\Rightarrow \sum_n a_n \left[\left\langle m \middle| \hat{\mathrm{H}} \middle| n \right\rangle - \lambda\delta_{mn}\right] = 0 \tag{45}$$

or

$$\left\langle m \middle| \left(\hat{\mathrm{H}} - \lambda\right) \sum_n a_n \middle| n \right\rangle \quad \forall m \Rightarrow \{a_m, \lambda\} \tag{46}$$

In this reduced basis in the original subspace of $\{a_m\}$

$$\sum_n a_n^{(i)} |n\rangle \tag{47}$$

are N linearly independent eigenvectors of $\hat{\mathrm{H}}$ with eigenvectors $E^{(i)} = \lambda^{(i)}$ Where $a^{n^{(i)}}$ is If picked well, the first few $E^{(i)}$ may be good estimate for first few energies.

Remark 3.4:1

We (the type-setter) also recommand checking out Wikipedia for good examples and more of a supplement for this.

4: Stationary State (TIPT)

4.1. The Idea

We'll now look at new type of approximation which relies on iterative steps towards the right answer. This encompasses Time-Independent Pertubation Theory (TIPT). We start by looking for a series expansion that converges for "small pertubations" on a Hamiltonian we've solved.

4.2. Formulation

Consider the Hamiltonian:

$$\hat{\mathrm{H}} = \hat{\mathrm{H}}_0 + \hat{\mathrm{V}} \tag{1}$$

where $\hat{\mathrm{H}}_0$ is a solved Hamiltonian, that is, we've solved already the Eigenstate problem for

$$\hat{\mathrm{H}}_0|n\rangle = \varepsilon_n|n\rangle \tag{2}$$

But we're now interested in solving the same problem for $\hat{\mathrm{H}}$. If $\hat{\mathrm{V}}$ is relatively small compared to the potential of $\hat{\mathrm{H}}_0$, call it $\hat{\mathrm{V}}_0$, then we expect that $|n\rangle$ and ε_n to be still approximate for $\hat{\mathrm{H}}$.

Warning 4.2:1 (Pertubation of a Free Particle)

Perturbing a free particle with *any* potential will always result in a bad answer. Any non-zero potential, $\hat{\mathrm{V}}$, will always be infinitely large compared to $\hat{\mathrm{V}}_0 = 0$.

Let

$$\hat{\mathrm{H}}(\lambda) = \hat{\mathrm{H}} + \lambda\hat{\mathrm{V}} \tag{3}$$

where $\lambda \in [0, 1]$. This variable allows us to "slowly turn on" the potential $\hat{\mathrm{V}}$ by letting it approach 1. We *expect* that our eigenstates will vary smoothly from $|n\rangle$ at $\lambda = 0$ to $|N\rangle$ at $\lambda = 1$, where $|N\rangle$ is the new eigenvector we wish to find.

That is:

$$\left(\hat{\mathrm{H}}_0 + \lambda\hat{\mathrm{V}}\right)|N\rangle = E_n|N\rangle \tag{4}$$

Let us now expand in powers of λ:

$$|N\rangle = |n\rangle + \lambda\left|N^{(1)}\right\rangle + \lambda^2\left|N^{(2)}\right\rangle + \ldots \tag{5}$$

$$E_n = \varepsilon_n + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots \tag{6}$$

Here, $\left|N^{(i)}\right\rangle$ and $E^{(i)}$ are the ith order correction terms for $\hat{\mathrm{V}}$.

Remark 4.2:2

What λ really is here is just a nice "book keeping" variable for powers of $\hat{\mathrm{V}}$. So λ^n should really be thought of as corresponding to $\hat{\mathrm{V}}^n$.

Without loss of generality, we may assume that the $|n\rangle$ is orthonormal and that $|N\rangle$ (not necessarily normalize) has a component of $|n\rangle$. Mathematically:

$$\langle n \,|\, m\rangle = \delta_{mn} \tag{7}$$

$$\langle n \,|\, N \rangle = 1 \tag{8}$$

Note that in general have:

$$\langle N \,|\, N \rangle \neq 1 \tag{9}$$

With this though we can continue:

$$\langle n \,|\, N \rangle = 1 = 1 + \lambda \langle n \,|\, N^{(1)} \rangle + \ldots \tag{10}$$

So $\langle n \,|\, N^{(i)} \rangle = 0$ for $i \neq 0$. By the Schrödinger Equation:

$$\left(\hat{\mathrm{H}}_0 + \lambda V\right)|N\rangle = E_n|N\rangle \tag{11}$$

$$\left(\hat{\mathrm{H}}_0 + \lambda V\right)\left[|n\rangle + \sum_i \lambda^i |N^{(i)}\rangle\right] \tag{12}$$

$$= \left[\varepsilon_0 + \sum_i \lambda^i E_n^{(i)}\right]\left[|n\rangle + \sum_i \lambda^i |N^{(i)}\rangle\right] \tag{13}$$

Equating powers of λ

$$\lambda^0 : \hat{\mathrm{H}}_0|n\rangle = \varepsilon_n|n\rangle \tag{14}$$

$$\lambda^1 : \hat{\mathrm{H}}_0|N^{(1)}\rangle + \hat{\mathrm{V}}|n\rangle = \varepsilon_n|N^{(1)}\rangle + E_n^{(1)}|n\rangle \tag{4.2:15}$$

$$\lambda^k : \hat{\mathrm{H}}_0|N^{(k)}\rangle + \hat{\mathrm{V}}|N^{(k-1)}\rangle = \sum_i^k E_n^{(i)}|N^{(k-i)}\rangle \tag{4.2:16}$$

where

$$E_n^{(0)} = \varepsilon_n \quad ; \quad |N^{(0)}\rangle = |n\rangle \tag{17}$$

This gives us enough to find all higher order corrections.

4.2.1. Energy Corrections

To find the first-order energy correction, we take the scalar product of **Equation (15)** with $\langle n|$

$$\left\langle n \,\middle|\, \hat{\mathrm{H}}_0 \,\middle|\, N^{(1)} \right\rangle + \left\langle n \,\middle|\, \hat{\mathrm{V}} \,\middle|\, n \right\rangle = \underbrace{\langle n \,|\, \varepsilon_n \,|\, N^{(1)} \rangle}_{0} + \underbrace{\left\langle n \,\middle|\, E_n^{(1)} \,\middle|\, n \right\rangle}_{E_n^{(1)}} \tag{18}$$

Where the first term was removed due to orthogonality. So we find that

$$E_n = \varepsilon_n + \left\langle n \,\middle|\, \hat{\mathrm{V}} \,\middle|\, n \right\rangle \quad ; \quad \left\langle n \,\middle|\, \hat{\mathrm{V}} \,\middle|\, n \right\rangle = E_n^{(1)} \tag{19}$$

For $k = 2$ we also have the helpful identity (that you can prove after **Section 4.2.2**):

$$E_n^{(k)} = \sum_{m \neq n} \frac{\left|\left\langle m \,\middle|\, \hat{\mathrm{V}} \,\middle|\, n \right\rangle\right|^2}{\varepsilon_n - \varepsilon_m} \tag{20}$$

In general, we do the same thing with **Equation (16)** to get:

$$E_n^{(k)} = \left\langle n \,\middle|\, \hat{\mathrm{V}} \,\middle|\, N^{(k-1)} \right\rangle \tag{21}$$

Thus if we know $(k-1)$-th order correction to the wave function, we can obtain the kth order correction to energy. Thus we now need a way to compute the wave function corrections.

4.2.2. Wave Function Corrections

We start by expanding in eigenstates of $\hat{\mathrm{H}}_0$:

$$\left|N^{(k)}\right\rangle = \sum_{m\neq n} |m\rangle\langle m\,|\,N^{(k)}\rangle \quad ; \quad k = 1, 2, \ldots \tag{22}$$

Where $m = n$ is excluded by orthogonality. We now take once again the scalar product of **Equation (16)** with $\langle m|$ to set expansion coefficients. For $m \neq n$:

$$\underbrace{\left\langle m\,\middle|\,\hat{\mathrm{H}}_0\,\middle|\,N^{(k)}\right\rangle}_{\left\langle \hat{\mathrm{H}}_0 m\,\middle|\,N^{(k)}\right\rangle = \varepsilon_m\langle m\,|\,N^{(k)}\rangle} + \left\langle m\,\middle|\,\hat{\mathrm{V}}\,\middle|\,N^{(k-1)}\right\rangle = \underbrace{\sum_i^k E_n^{(i)}\langle m\,|\,N^{(k-i)}\rangle}_{\varepsilon_n\langle m\,|\,N^{(k)}\rangle + \sum_i^{k-1} E_n^{(i)}\langle m\,|\,N^{k-i}\rangle} \tag{23}$$

$$\left\langle m\,\middle|\,N^{(k)}\right\rangle = \frac{1}{\varepsilon_n - \varepsilon_m}\left[\left\langle m\,\middle|\,\hat{\mathrm{V}}\,\middle|\,N^{(k-1)}\right\rangle - \sum_i^{k-1} E_n^{(i)}\langle m\,|\,N^{k-i}\rangle\right] \tag{24}$$

So for first order, $k = 1$, we have

$$\left\langle m\,\middle|\,N^{(1)}\right\rangle = \frac{1}{\varepsilon_n - \varepsilon_m}\left\langle m\,\middle|\,\hat{\mathrm{V}}\,\middle|\,n\right\rangle \tag{25}$$

4.3. Examples

Example 4.3:1 (Helium Ground State)

Let $\hat{\mathrm{H}}_H$ be the Hydrogen hamiltonian and $\hat{\mathrm{V}} = \frac{\alpha}{R}$ where $\boldsymbol{R} = \boldsymbol{r}_1 - \boldsymbol{r}_2$ and $R = \|\boldsymbol{R}\|$. We have for the Helium atom:

$$\hat{\mathrm{H}} = \hat{\mathrm{H}}_H + \hat{\mathrm{V}} \tag{26}$$

We know the ground state for $\hat{\mathrm{H}}_H$ is just

$$|n = 0\rangle = \frac{Z^3}{\pi a_0^3} e^{-\frac{Z}{a_0}(r_1 + r_2)} \quad ; \quad Z = 2 \tag{27}$$

with

$$\varepsilon_0 = -\frac{1}{2} m\alpha^2 [2Z^2] \approx -108.9\,eV \tag{28}$$

Now we calculate the first order ground state energy correction:

$$E_0^{(1)} = \left\langle n = 0\,\middle|\,\hat{\mathrm{V}}\,\middle|\,n = 0\right\rangle \tag{29}$$

$$= \int_\infty \mathrm{d}^3(\boldsymbol{x}) \int_\infty \mathrm{d}^3(y) \left(\frac{Z^3}{\left(\pi a_0^3\right)^2}\right) \exp\left(-\frac{2Z}{a_0}(r_1 + r_2)\right) \tag{30}$$

Which we evaluated from a previous leture:

$$\Rightarrow E_0^{(1)} = \frac{1}{2} m\alpha^2 \left[\frac{5}{4} Z\right]_{Z=2} \approx 34.0\,eV \tag{31}$$

$$E_0 = \varepsilon_0 + E_0^{(1)} + O\left(\hat{\mathrm{V}}^2\right) \quad ; \quad \text{Formally, } \hat{\mathrm{V}}^2 \text{ here means } \lambda^2 \tag{32}$$

$$E_0 \approx -74.9\,eV \tag{33}$$

This result is $3.7\,eV$ away from the experimental value, $-78.6\,eV$, so we were off by -4.7%. Note that this result is worse than the variational approach we did in **Example 3.2.1**. This should be expected, as our first order correction was calculated to be $+34eV$, a rather larger correction compared to the unperturbed $-109eV$. More or less, these two calculations were the same, except in this one we didn't allow Z to vary.

5: More TIPT

5.1. Normalization

Recall that we chose $\langle n \,|\, N\rangle = 1$ to make the expansion convenient in **Section 4.2**. Of course, we'd like to know how to normalize this wave function, and it turns out to be particularly easy because of our convention. Let our normalized wave function be

$$\left|\widehat{N}\right\rangle = \sqrt{A}|N\rangle \quad ; \quad \left\langle \widehat{N} \,\middle|\, \widehat{N}\right\rangle = 1 \tag{1}$$

Therefore we have:

$$A = \frac{1}{\langle N \,|\, N\rangle} \tag{2}$$

which is sometimes called the "*wave renormalization constant*." Also recognize the handy identity:

$$\left\langle n \,\middle|\, \widehat{N}\right\rangle = \sqrt{A}\langle n \,|\, N\rangle = \sqrt{A} \tag{3}$$

Thus to second order:

$$\frac{1}{A} = \langle N \,|\, N\rangle = \left(\langle n| + \lambda\left\langle N^{(1)}\right| + \lambda^2\left\langle N^{(2)}\right|\right)\left(|n\rangle + \lambda\left|N^{(1)}\right\rangle + \lambda^2\left|N^{(2)}\right\rangle\right) + O(\lambda^3) \tag{4}$$

$$= 1 + \lambda^2 \sum_{m\neq n} \frac{\left|\left\langle m \,\middle|\, \hat{\mathrm{V}} \,\middle|\, n\right\rangle\right|^2}{\left(\varepsilon_n - \varepsilon_m\right)^2} + \ldots \tag{5}$$

Which implies that, to first order, $|N\rangle$ is already normalized to one. Corrections only appear at the next order. To second order, we have

$$A = 1 - \lambda^2 \sum_{m\neq n} \frac{\left|\left\langle m \,\middle|\, \hat{\mathrm{V}} \,\middle|\, n\right\rangle\right|^2}{\left(\varepsilon_n - \varepsilon_m\right)^2} - O(\lambda^3) \tag{6}$$

$$= \frac{\partial}{\partial \varepsilon_n}\left(\varepsilon_n + \lambda \underbrace{\langle n|\hat{\mathrm{V}}|n\rangle}_{\frac{\partial}{\partial\varepsilon_n}=0} + \lambda^2 \sum_{m\neq n} \frac{\left|\left\langle m \,\middle|\, \hat{\mathrm{V}} \,\middle|\, n\right\rangle\right|^2}{\varepsilon_n - \varepsilon_m}\right) - O(\lambda^3) \tag{7}$$

$$= \frac{\partial E_n}{\partial \varepsilon_n} - O(\lambda^3) \tag{8}$$

It turns out this result is valid for all orders in pertubation theory. If a system is in eigenstate $\left|\widehat{N}\right\rangle = \sqrt{A}|N\rangle$, the probability, A, to observe it in the unperturbed state $|n\rangle$ is just the partial derivative of the perturbed energy with respect to the unperturbed energy (keeping ε_m for $m \neq n$, and $\left\langle m \,\middle|\, \hat{\mathrm{V}} \,\middle|\, n\right\rangle$ fixed).

5.1.1. Example

Example 5.1:1

Let $\hat{\mathrm{H}}_0$ be a 1D quantum harmonic oscillator potential and

$$\hat{\mathrm{H}} = \hat{\mathrm{H}}_0 + \rho\omega\hat{\mathrm{X}} \quad \text{where} \quad \rho \ll 1 \tag{9}$$

It can be shown that

$$\hat{\mathrm{V}} = \rho\frac{\omega}{\sqrt{2}}(a^\dagger + a) \tag{10}$$

Our pertubation expansion for the energy level is:

$$E_n = \varepsilon_n + \langle n|\hat{\mathrm{V}}|n\rangle + \sum_{m\neq n}\frac{\left|\left\langle m\,\middle|\,\hat{\mathrm{V}}\,\middle|\,n\right\rangle\right|^2}{\varepsilon_n - \varepsilon_m} + \ldots \tag{11}$$

Since $V \propto (a^\dagger + a)$, the only non-vanishing matrix elements are $\left\langle n+1\,\middle|\,\hat{\mathrm{V}}\,\middle|\,n\right\rangle$ and $\left\langle n-1\,\middle|\,\hat{\mathrm{V}}\,\middle|\,n\right\rangle$. In particular, the first order correction $\langle n|\hat{\mathrm{V}}|n\rangle = 0$.

We evaluate

$$\langle n-1\,|\,V\,|\,n\rangle = \rho\frac{\omega}{\sqrt{2}}\langle n-1\,|\,a\,|\,n\rangle = \rho\frac{\omega}{\sqrt{2}}\sqrt{n} \tag{12}$$

$$\langle n-1\,|\,V\,|\,n\rangle = \rho\frac{\omega}{\sqrt{2}}\langle n+1\,|\,a\,|\,n\rangle = \rho\frac{\omega}{\sqrt{2}}\sqrt{n+1} \tag{13}$$

with $\varepsilon_n - \varepsilon_{n\pm1} = \mp\omega$. This gives us

$$E_n = \left(n + \frac{1}{2}\right)\omega - \frac{\rho^2}{2}\omega \tag{14}$$

It turns out this is the exact solution, and we'd discover that all higher-order corrections vanish.

Solving for the first-order corrections to $|n\rangle$, we have:

$$\left\langle m\,\middle|\,N^{(1)}\right\rangle = \frac{\left\langle m\,\middle|\,\hat{\mathrm{V}}\,\middle|\,n\right\rangle}{\varepsilon_n - \varepsilon_m} \tag{5.1:15}$$

Hence

$$|N\rangle = |n\rangle + \sum_{m\neq n}|m\rangle\frac{\left\langle m\,\middle|\,\hat{\mathrm{V}}\,\middle|\,n\right\rangle}{\varepsilon_n - \varepsilon_m} + \ldots \tag{16}$$

$$= |n\rangle - \rho\sqrt{\frac{n-1}{2}}|n+1\rangle + \rho\sqrt{\frac{n}{2}}|n-1\rangle + \ldots \tag{17}$$

5.2. Degeneracy

If $\varepsilon_n = \varepsilon_m$ and $\left\langle n\,\middle|\,\hat{\mathrm{V}}\,\middle|\,m\right\rangle \neq 0$, then we notice that our above formulation breaks down, namely since **Equation (5.1.15)** will diverge. It turns out however that we can salvage this. Suppose that a set of states:

$$|n_1\rangle, |n_2\rangle, \ldots, |n_k\rangle \quad \text{¦} \quad \text{degenerate with respect to } \hat{\mathrm{H}}_0 \tag{18}$$

that is

$$\hat{\mathrm{H}}_0|n_i\rangle = \varepsilon_n|n_i\rangle \quad ; \quad \forall i \tag{19}$$

If $\left\langle n_i\,\middle|\,\hat{\mathrm{V}}\,\middle|\,n_j\right\rangle \neq 0$ for $i \neq j$, then as we've mentioned, our theory fails. However we can choose *any* linear combination of these states and we'll remain in the same eigenspace. That is, any linear com-

bination of these states also has the same energy eigenvalues, so we can try choosing a new basis. Namely, one that diagonalizes $\hat{\mathrm{V}}$ in this subspace:

$$|n_i'\rangle = \sum_{j=1}^{k} \hat{\mathrm{C}}_{ij}|n_j\rangle \quad ; \quad \left\langle n_i' \middle| \hat{\mathrm{V}} \middle| n_j' \right\rangle = 0 \tag{20}$$

Where the matrix $\hat{\mathrm{C}}$ which does this is just the matrix formed by the normalized eigenvectors of the $\hat{\mathrm{V}}$ matrix:

$$\hat{\mathrm{V}}_{ij} = \left\langle n_i \middle| \hat{\mathrm{V}} \middle| n_j \right\rangle \tag{21}$$

$$\hat{\mathrm{V}}\hat{\mathrm{C}}_j = \lambda_j \hat{\mathrm{C}}_j \quad ; \quad \sum_{j=1}^{k} \left| \left(\hat{\mathrm{C}}_j\right)_i \right|^2 = 1 \tag{22}$$

$$\Rightarrow |n_i'\rangle = \sum_{j=1}^{k} \left(\hat{\mathrm{C}}_i\right)_j |n_j\rangle = \left|\hat{\mathrm{C}}_i\right\rangle \tag{23}$$

One can check that

$$\left\langle n_i' \middle| \hat{\mathrm{V}} \middle| n_j' \right\rangle = \delta_{ij}\lambda_j \tag{24}$$

Now we have the orignal 1st order PT results:

$$|N_i'\rangle = |n_i'\rangle + \sum_{m \notin \mathrm{span}\{n_k\}_k} \frac{\left\langle m \middle| \hat{\mathrm{V}} \middle| n_i' \right\rangle}{\varepsilon_n - \varepsilon_m} |m\rangle + \ldots \tag{25}$$

and

$$E_{n_i'} = \varepsilon_n + \left\langle n_i' \middle| \hat{\mathrm{V}} \middle| n_i' \right\rangle + \sum_{m \notin \mathrm{span}\{n_k\}_k} \frac{\left| \left\langle m \middle| \hat{\mathrm{V}} \middle| n_i' \right\rangle \right|^2}{\varepsilon_n - \varepsilon_m} + \ldots \tag{26}$$

Observe that $E_{n_i'}$ does depend on i in general. The implications of this is that $\hat{\mathrm{V}}$ can cause a symmetry breaking on the degenerate eigenspace, allowing them to have different eigenvalues. Let's see an example of this in action.

Example 5.2:1 (Degeneracy Example)

Let

$$\hat{\mathrm{H}}(\lambda) = \hat{\mathrm{H}}_0 + \lambda\hat{\mathrm{V}} \tag{27}$$

with $\hat{\mathrm{H}}_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ and $\hat{\mathrm{V}} = \delta\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$. And notice that we can solve the eigen problem for both Hamiltonians. For $\hat{\mathrm{H}}_0$ we have:

$$|1\rangle_0 = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad ; \quad |2\rangle_0 = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{28}$$

And for our first order correction we see:

$$E_1^{(1)} = \left\langle 1|_0 \hat{\mathrm{V}} \middle| 1 \right\rangle_0 = (1,0)\hat{\mathrm{V}}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0 \tag{29}$$

$$E_2^{(1)} = \left\langle 2|_0 \hat{\mathrm{V}} \middle| 2 \right\rangle_0 = (0,1)\hat{\mathrm{V}}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = 0 \tag{30}$$

So we have

$$E_1 = 1 + \lambda 0 + O(\lambda^2) \tag{31}$$

$$E_2 = 1 + \lambda 0 + O(\lambda^2) \tag{32}$$

But now solving for $\hat{\mathrm{H}}$, we have

$$\hat{\mathrm{H}}(\lambda) = \begin{pmatrix} 1 & \lambda\delta \\ \lambda\delta & 1 \end{pmatrix} \tag{33}$$

with eigenstates

$$|1\rangle_{\hat{\mathrm{H}}} = \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad ; \quad |2\rangle_{\hat{\mathrm{H}}} = \begin{pmatrix} 1 \\ -1 \end{pmatrix} \tag{34}$$

with eigenvalues

$$1 \pm \lambda\delta + O(\lambda^2) \tag{35}$$

But this does have a non-zero first order term, unlike what we just calculated. Why was our first set wrong? The problem lies in the fact that our pertubation potential, $\hat{\mathrm{V}}$, broke the symmetry of the degeneracy. For *any* $\lambda > 0$, our eigenvectors break non-continuously. We can also see the pathology again by **Equation (5.1.15)**,

$$\langle 2|_0 N^{(1)} \rangle = \frac{\delta}{\varepsilon_1 - \varepsilon_2} = \frac{\delta}{0} = \infty \tag{36}$$

This however can be solved if we instead choose eigenvectors of $\hat{\mathrm{H}}_0$ that are still eigenvectors of $\hat{\mathrm{V}}$. In this case, $|1\rangle_{\hat{\mathrm{H}}}$ and $|2\rangle_{\hat{\mathrm{H}}}$. This will in general be true because for any degenerate eigenspace, any linear combination of $|1\rangle_0$ and $|2\rangle_0$ will always be an eigenvector, and it turns out we can always choose a "nice" set of eigenvectors. With this in mind:

$$\langle 1|_{\hat{\mathrm{H}}} \hat{\mathrm{V}} \,|\, 1\rangle_{\hat{\mathrm{H}}} = 1 + \lambda\delta + O(\lambda^2) \tag{37}$$

$$\langle 2|_{\hat{\mathrm{H}}} \hat{\mathrm{V}} \,|\, 2\rangle_{\hat{\mathrm{H}}} = 1 - \lambda\delta + O(\lambda^2) \tag{38}$$

Which is indeed correct.

6: Spin-Orbit Coupling

Refer to the text's pg 476 - 470 for more information. We will now consider a "spin-orbit coulping" in atomic physics, where the magnetic field from the electrons motion interacts with the magnetic moment of the electron due to its spin.

Remark 6.0:1 (Is this self-interaction?)

You could indeed call this self-interaction. Prof. Frank was a bit hesitant about it due to the fact that he seemed to suggest it was more of the field interacting. We could also get a similar answer from not treating it as a self-interaction, but instead using a potential from the magnetic moment of the nucleus.

This is typically a small effect and therefore it turns out to be an excellent model for pertubation theory. The pertubation Hamiltonian for hydrogen is

$$\hat{\mathrm{H}}_{\mathrm{SO}} = \frac{\alpha}{2m^2r^3}\hat{\mathbf{L}}\cdot\hat{\mathbf{S}} \tag{1}$$

Remark 6.0:2

It's unsurprising to see $1/r^3$ as this is the classical result of a dipole moment.

To first order and up to issues of degeneracy:

$$E^{(1)}_{nlm_lm_s} = \left\langle \psi_{nlm_lm_s} \middle| H_{\mathrm{SO}} \middle| \psi_{nlm_lm_s} \right\rangle \tag{2}$$

where the quantum numbers (QNs) are

$$n = \text{energy QN} \tag{3}$$

$$l = \text{angular momentum QN} \tag{4}$$

$$m_l = \text{orbital magnetic QN} \tag{5}$$

$$m_s = \text{spin} \tag{6}$$

Remark 6.0:3

This set of quantum numbers, n, l, m_l, m_s, is called the "*uncoupled representation.*"

where

$$\psi_{nlm_lm_s} = R_{nl}(r)Y_{lm_l}(\Omega)\chi_{m_s}(\Omega) \tag{7}$$

with $\Omega = (\theta, \varphi)$

$$E_n = \frac{1}{2}m\alpha^2\frac{1}{n^2} \tag{8}$$

where the degeneracy is $2n^2$, the factor of 2 coming from the fact that $\hat{\mathrm{H}}_0$ doesn't break the symmetry of m_s (it doesn't care if it's spin-up or down) and it doesn't break the symmetry of l and m_l, for which $0 \leq l \leq n$ and $-l \leq m_l \leq +l$, giving n^2 degeneracies.

Conisder now $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ with

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}} \tag{9}$$

Squaring, we have:

$$\hat{\mathbf{J}}^2 = \hat{\mathbf{L}}^2 + \hat{\mathbf{S}}^2 + 2\overline{\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}} \tag{10}$$

or

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{1}{2}\left(\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2\right) \tag{11}$$

$$\Rightarrow \hat{\mathrm{H}}_{\mathrm{SO}} = \frac{\alpha}{4mr^3}\left(\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2\right) \tag{12}$$

Here, $\hat{\mathbf{J}}, \hat{\mathbf{L}} + \hat{\mathbf{S}}$ suggest we should work in the QN basis, n, j, l, s, m_j where $m_j = m_l + m_s$. This gives

$$E^{(1)}_{nlj} = \frac{\alpha}{4m^2}\int_0^\infty r^2 \mathrm{d}r \frac{1}{r^3}|R_{nl}(r)|^2 \left\langle \hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2 \right\rangle \tag{13}$$

We notice that in this basis there's no dependence on m_l, m_s.

The matrix elements between angular momentum states are

$$\left\langle j', m_{j'}, l', s' = \frac{1}{2} \right| H_{\mathrm{SO}} \left| j, m_j, l, s = \frac{1}{2} \right\rangle \tag{14}$$

$$= \delta_{jj'}\delta_{ll'}\delta_{ss'}\delta_{mm'}\frac{\alpha}{4m^2}\left\langle \frac{1}{r^3} \right\rangle_{nl} \left(j(j+1) - l(l+1) - \underbrace{s(s+1)}_{3/4} \right) \tag{15}$$

Notice that we have delta functions for every QN, implying we've already diagonalized the matrix in this basis. But

$$j = l \pm \frac{1}{2} > 0 \tag{16}$$

hence

$$j(j+1) = \left(l \pm \frac{1}{2}\right)\left(l + 1 \pm \frac{1}{2}\right) = l(l+1) + \frac{1}{4} \pm l \pm \frac{1}{2} \tag{17}$$

therefore

$$j(j+1) - l(l+1) - \frac{3}{4} = \{l, -(l+1)\} \begin{cases} l & ; \quad j = l + \frac{1}{2} \\ -(l+1) & ; \quad j = l - \frac{1}{2} \end{cases} \tag{18}$$

$$\Rightarrow E^{(1)}_{nl} = \frac{\alpha}{4m^2}\left\langle \frac{1}{r^3} \right\rangle_{nl} j(j+1) \tag{19}$$

With the claim that

$$\left\langle \frac{1}{r^3} \right\rangle_{nl} = \frac{1}{\alpha_0^3}\frac{1}{n^3 l\left(l + \frac{1}{2}\right)(l+1)} \tag{20}$$

$$\Rightarrow E^{(1)}_{nl} = \frac{1}{4}m\alpha^4 \frac{1}{n^3\left(l + \frac{1}{2}\right)(l+1)} \quad \text{or} \quad \frac{1}{4}m\alpha^4 \frac{-1}{n^3 l\left(l + \frac{1}{2}\right)} \tag{21}$$

But what about $l = 0$? We have $\langle L \cdot S \rangle = 0$ but $\left\langle \frac{1}{r^2} \right\rangle = \infty$. If we naively applied the formula, we would get:

$$E_{n0}^{(1)} = \frac{m\alpha^4}{2n^3} \tag{22}$$

which in fact is correct, but we would like to have used the Dirac Equation to ensure this is correct.

We note that we did not need to worry about degeneracies because $\boldsymbol{H}_{\text{SO}}$ is diagonal in the basis

$$|nlsjm_j\rangle \tag{23}$$

the so-called "coupled representation."

Remark 6.0:4

This is an entire factor of α^2 smaller than the unperturbed energy levels. This sort of energy-splitting is called the "fine structure" of the atom.

7: Time-Dependent PT

So far we've been talking about time-independent pertubation theory. Last time it was about degenerate wave functions but now we'll introduce a time-dependence on our potential function.

Suppose at time $t < t_0$, the system is stable with $|\psi_t^0\rangle$ satisfying the Schrödinger equation with

$$i\partial_t|\psi_t^0\rangle = \hat{\mathrm{H}}_0|\psi_t^0\rangle \tag{1}$$

At $t = t_0$, we turn on a pertubing potential, $\hat{\mathrm{V}}_t$ which we wish to solve the Schrödinger equation for, for $t > t_0$. We have:

$$i\partial_t|\psi_t\rangle = \left(\hat{\mathrm{H}}_0 + V_t\right)|\psi_t\rangle \quad ; \quad t > t_0 \tag{2}$$

We'll need $\hat{\mathrm{V}}_t$ to be "small enough" such that we can find a valid enough approximation, and we likewise look for an expansion in powers of $\hat{\mathrm{V}}_t$ like we did for stationary state approximation. Note that $|\psi_t\rangle$ contains a t-dependence from $\hat{\mathrm{H}}_0$ as a solution to the Schrödinger Equation (and not the time-independent Schrödinger equation). If $\hat{\mathrm{H}}_0 \gg V_t$, we expect that this is a large portion of the total t dependence. We take this out to streamline our calculations.

We define

$$|\psi_t\rangle := e^{-i\hat{\mathrm{H}}_0 t}|\psi(t)\rangle \tag{3}$$

Remark 7.0:1

The definitions of each are different and it's important to note that if $|\psi\rangle$ has parantheses, then it's missing a factor of $e^{-i\hat{\mathrm{H}}_0 t}$. Note that $|\psi_t\rangle$ is the solution to the time-independent Schrödinger equation.

With this,

$$i\partial_t|\psi_t\rangle = i\partial_t\left(e^{-i\hat{\mathrm{H}}_0 t}|\psi(t)\rangle\right) \tag{4}$$

$$= \hat{\mathrm{H}}_0|\psi_t\rangle + e^{-i\hat{\mathrm{H}}_0 t}\partial_t|\psi(t)\rangle \tag{5}$$

$$= \left(\hat{\mathrm{H}}_0 + V_t\right)|\psi_t\rangle \tag{6}$$

$$= V_t e^{-i\hat{\mathrm{H}}_0 t}|\psi(t)\rangle \tag{7}$$

or

$$i\partial_t|\psi(t)\rangle = \underbrace{e^{i\hat{\mathrm{H}}_0 t}V_t e^{-i\hat{\mathrm{H}}_0 t}}_{\hat{\mathrm{V}}(t)}|\psi(t)\rangle \tag{8}$$

$$\hat{\mathrm{V}}(t) := e^{i\hat{\mathrm{H}}_0 t}V_t e^{-i\hat{\mathrm{H}}_0 t} \tag{9}$$

We call $|\psi(t)\rangle$, the state vector, in the "interaction representation," suggesting time dependence is only due to the pertubation.

Remark 7.0:2 (The Heisenberg Picture)

In the Heisenberg picture, we move the time-dependence of the Schrödinger equation and the wave functions to the operators. Here we are doing the same thing except introducing the potential $\hat{V}_t$ as well. If $\hat{V}_t = 0$, then we have the Heisenberg picture.

Now we integrate w.r.t. to t.

$$\int_{t_0}^{t} \partial_{t_1} |\psi(t_1)\rangle \mathrm{d}t_1 = |\psi(t)\rangle - |\psi(t_0)\rangle \tag{10}$$

to

$$\Rightarrow |\psi(t)\rangle = |\psi(t_0)\rangle + \frac{1}{i}\int_{t_0}^{t} \hat{V}(t_1)|\psi(t_1)\rangle \mathrm{d}t' \tag{7.0:11}$$

Which suggests an iterative solution. To first order we write:

$$|\psi(t)\rangle = |\psi(t_0)\rangle + \frac{1}{i}\int_{t_0}^{t} \hat{V}(t_1)|\psi(t_1)\rangle \mathrm{d}t_1 \tag{7.0:12}$$

To find 2nd order, we subsitute the last two equations in each other:

$$\begin{aligned} |\psi(t)\rangle &= |\psi(t_0)\rangle + \frac{1}{i}\int_{t_0}^{t} \hat{V}(t_1)|\psi(t_1)\rangle \mathrm{d}t_1 \\ &+ \left(\frac{1}{i}\right)^2 \int_{t_0}^{t} \mathrm{d}t_1 \hat{V}(t_1) \int_{t_0}^{t_1} \mathrm{d}t_2 \hat{V}(t_2)|\psi(t_0)\rangle \end{aligned} \tag{13}$$

In general the nth order correction is:

$$\left|\psi(t)^{(n)}\right\rangle = \frac{1}{i^n}\int_{t_0}^{t} \mathrm{d}t_1 \ldots \int_{t_0}^{t_{n-1}} \mathrm{d}t_n \hat{V}(t_1)\ldots\hat{V}(t_0)|\psi(t_0)\rangle \tag{14}$$

Warning 7.0:3

We are not guaranteed to converge. We can be guaranteed a convergence with some special restrictions on $\hat{V}$ however.

7.1. Path Integrals

We first define a "time-ordered product." We need it to be time ordered because linear transformations/matrices do not necessarily commute. The notation will either be:

$$\Big\{ \qquad \Big\}_t \text{ or } T \text{ or } \mathcal{T} \tag{15}$$

Defining it:

$$\{A(t_1)B(t_2)\}_t \equiv \begin{cases} A(t_1)B(t_2) & t_1 \geq t_2 \\ B(t_2)A(t_1) & t_1 \leq t_2 \end{cases} \tag{16}$$

Where A and B are operators and thus not necessarily commuting.

7.1.1. Connecting to TDPT

Consider

$$\left\{\left[\int_{t_0}^{t}\hat{\mathrm{V}}(t_1)\mathrm{d}t_1\right]^2\right\}= \tag{17}$$

$$\int_{t_0}^{t}\mathrm{d}t_1\int_{t_0}^{t}\mathrm{d}t_2\left\{\hat{\mathrm{V}}(t_1)\hat{\mathrm{V}}(t_2)\right\}_t \tag{18}$$

$$\int_{t_0}^{t}\mathrm{d}t_1\int_{t_0}^{t_1}\mathrm{d}t_2\hat{\mathrm{V}}(t_1)\hat{\mathrm{V}}(t_2)+\int_{t_0}^{t}\mathrm{d}t_2\int_{t_0}^{t_2}\mathrm{d}t_1\hat{\mathrm{V}}(t_2)\hat{\mathrm{V}}(t_1) \tag{19}$$

$$2\int_{t_0}^{t}\mathrm{d}t_1\int_{t_0}^{t_1}\mathrm{d}t_2\hat{\mathrm{V}}(t_1)\hat{\mathrm{V}}(t_2) \tag{20}$$

Which is twice our second-order correction (if we multiply it by $|\psi(t)\rangle$). This suggests, and it does indeed generalize, that:

$$\left\{\left[\int_{t_0}^{t}\mathrm{d}t_1\hat{\mathrm{V}}(t_1)\right]^n\right\}_t=\int_{t_0}^{t}\mathrm{d}t_1\ldots\int_{t_0}^{t_n}\mathrm{d}t_n\left\{\hat{\mathrm{V}}_{t_1}\hat{\mathrm{V}}_{t_2}\ldots\hat{\mathrm{V}}(t_n)\right\}_t \tag{21}$$

$$=n!\int_{t_0}^{t}\mathrm{d}t_1\ldots\int_{t_0}^{t_n}\mathrm{d}t_n\hat{\mathrm{V}}(t_1)\hat{\mathrm{V}}_{t_2}\ldots\hat{\mathrm{V}}(t_n) \tag{22}$$

Thus

$$\frac{1}{i^n n!}\left\{\left[\int_{t_0}^{t}\hat{\mathrm{V}}(t_1)\mathrm{d}t_1\right]^n\right\}_t|\psi(t_0)\rangle \tag{23}$$

is our nth order correction term in the expansion. Assuming convergence, we have:

$$\Rightarrow|\psi(t)\rangle=\left\{\exp\left[-i\int_{t_0}^{t}\hat{\mathrm{V}}(t_1)\mathrm{d}t_1\right]\right\}_t|\psi(t_0)\rangle \tag{24}$$

7.2. Examples

Example 7.2:1

Suppose initially that for $t=t_0$, the system is in an eigenstate $|i\rangle$ of $\hat{\mathrm{H}}_0$. That is

$$|\psi(t_0)\rangle=|i\rangle \tag{25}$$

where

$$\hat{\mathrm{H}}_0|i\rangle=\varepsilon_i|i\rangle \tag{26}$$

Warning 7.2:2

$|i\rangle$ and $|t\rangle$ are written in interaction representation.

Let $|n\rangle$ denote an arbitrary eigenstate of $\hat{\mathrm{H}}_0$. We ask the question, at $t>t_0$, what is the probability that the system will be observed in state $|n\rangle$. I.e. what is the probability that the interaction has caused a measurable transition, $|i\rangle\to|n\rangle$. Note that we do not need to be able to measure $|n\rangle$ directly to acknowledge that this number is important. It is related to the coefficient expansion in the basis of $|i\rangle$, ..., $|n\rangle$, etc, which is an important enough of a topic to warrant this question.

In interaction representation, the amplitude is $\langle n \,|\, \psi(t)\rangle$. To first order:

$$\langle n \,|\, \psi(t)\rangle = \langle n \,|\, i\rangle + \frac{1}{i}\int_{t_0}^{t} \mathrm{d}t_1 \left\langle n \,\middle|\, \hat{\mathrm{V}}(t_1) \,\middle|\, i\right\rangle \tag{27}$$

but

$$\left\langle n \,\middle|\, \hat{\mathrm{V}}(t_1) \,\middle|\, i\right\rangle = \left\langle n \,\middle|\, e^{i\hat{\mathrm{H}}_0 t_1}\hat{\mathrm{V}}_{t_1} e^{-i\hat{\mathrm{H}}_0 t_1} \,\middle|\, i\right\rangle \tag{28}$$

$$= e^{i(\varepsilon_n - \varepsilon_i)t_1}\left\langle n \,\middle|\, \hat{\mathrm{V}}_{t_1} \,\middle|\, i\right\rangle \tag{29}$$

Hence if $|n\rangle \neq |i\rangle$, or more accurately, if $\langle n \,|\, i\rangle = 0$, then the transition amplitude is:

$$\langle n \,|\, \psi(t)\rangle = \frac{1}{i}\int_{t_0}^{t} \mathrm{d}t_1 e^{i(\varepsilon_n - \varepsilon_i)t_1}\left\langle n \,\middle|\, \hat{\mathrm{V}}_{t_1} \,\middle|\, i\right\rangle \tag{30}$$

and the transitional probability is $|\langle n \,|\, \psi(t)\rangle|^2$.

Example 7.2:3

Suppose

$$\hat{\mathrm{V}}_t = \begin{cases} 0 & ; \quad t < t_0 = 0 \\ \hat{\mathrm{V}}_1 & ; \quad t > 0 \end{cases} \tag{31}$$

Where $\hat{\mathrm{V}}_1$ has no time dependence. A so called "*sudden pertubation.*" Then

$$\mathbb{P}[i \to n; t] = \left| \int_0^t \mathrm{d}t_1 e^{i(\varepsilon_n - \varepsilon_i)t_1} \underbrace{\left\langle n \,\middle|\, \hat{\mathrm{V}} \,\middle|\, i\right\rangle}_{\text{no } t \text{ dependence}} \right|^2 \tag{32}$$

$$= \left| \frac{e^{i(\varepsilon_n - \varepsilon_i)t} - 1}{\varepsilon_n - \varepsilon_i}\left\langle n \,\middle|\, \hat{\mathrm{V}} \,\middle|\, i\right\rangle \right|^2 \tag{33}$$

$$= \left(\frac{2\sin\left(\frac{\varepsilon_n - \varepsilon_i}{2}t\right)}{\varepsilon_n - \varepsilon_i}\right)^2 \left|\left\langle n \,\middle|\, \hat{\mathrm{V}} \,\middle|\, i\right\rangle\right|^2 \tag{7.2:34}$$

or

$$= t^2 \mathrm{sinc}\left(\frac{\varepsilon_n - \varepsilon_i}{2}t\right)^2 \left|\left\langle n \,\middle|\, \hat{\mathrm{V}} \,\middle|\, i\right\rangle\right|^2 \tag{35}$$

Let's get an idea of what this transition probability looks like as a function of ε_n:

With $\varepsilon_n = \varepsilon_i$, we have

$$\mathbb{P}[i \to n; t] \approx t^2 \left|\left\langle n \,\middle|\, \hat{\mathrm{V}} \,\middle|\, i\right\rangle\right|^2 \tag{36}$$

Remark 7.2:4

We arrive at the same result if we replace $\varepsilon_n = \varepsilon_i$ with t very small by a Taylor Series approximation.

At $(\varepsilon_n - \varepsilon_i)/2t = k\pi$

$$\mathbb{P}[i \to n; t] = 0 \tag{37}$$

The last examples show us that for t very small, we have:

$$\mathbb{P}[i \to n; t] = t^2 \left| \left\langle n \left| \hat{\mathrm{V}} \right| i \right\rangle \right|^2 \tag{38}$$

which is independent of $\varepsilon_n - \varepsilon_i$ if $\left| \left\langle n \left| \hat{\mathrm{V}} \right| i \right\rangle \right|^2$ itself is not steeply dependent on it. As t increases, the probability is largest for states with ε_n near ε_i. This can be seen by the fact that the "height" of the probability (as a function of ε_n) is $\propto t^2$ while the width goes like $\propto 1/t$. In particular, the probability to be in the central "bump" is $\propto t$.

This can be thought of in terms of the energy-time uncertainty relation. If the pertubation turns on, or acts in a very short time, Δt, transitions may be induced in first order to a wide range of energy states:

$$\Delta\varepsilon\Delta t \underbrace{\geq}_{\substack{\text{since transition outside} \\ \text{of central bump is likely}}} \frac{\tau}{\Delta t}\Delta t = \tau \tag{39}$$

But as the transition is turned on more slowly, or has acted for a larger time, the uncertainty in the energy reduced by the pertubation decreases, i.e. is conserved to within $\Delta\varepsilon \sim \frac{\tau}{t}$.

If the levels $\varepsilon_n, \varepsilon_i$ are discrete, and $\varepsilon_n \neq \varepsilon_i$, the transition probability simply oscillates with period

$$T = \frac{\tau}{|\varepsilon_n - \varepsilon_i|} \tag{40}$$

If $|i\rangle$ and $|n\rangle$ are degenerate, then the probability grows as t^2. This cannot continue indefinitely since the probability must be less than 1. Eventually, higher orders in the pertubation do become important. Consider the case where $|n\rangle$ is drawn from a continuum of energy states, or, at least a spectrum of closely spaced levels, (e.g. a free particle). Then it makes more sense to ask for the transition probability to some set of states in the neighborhood of $|n\rangle$.

E.g., for a free particle, we want the transition probability to phase space element $\mathrm{d}^3(p)$ around p. Since the area of the central bump goes as t, we expect the transition probability to a set of such states with $\varepsilon_n \approx \varepsilon_i$ to grow linearly with time. Hence the transition *rate* to such a set of states is constant. Let us calculate the transition rate for this case.

We must sum **Equation (34)** over the region of interest (ROI):

$$\sum_{n\in \text{ ROI}} \mathbb{P}[i \to n; t] = \int_{\text{ROI}} \mathrm{d}\varepsilon_n \rho(\varepsilon_n) \left(\frac{2\sin\left(\frac{\varepsilon_n - \varepsilon_i}{2} t\right)}{\varepsilon_n - \varepsilon_i} \right)^2 \left| \left\langle n \left| \hat{\mathrm{V}} \right| i \right\rangle \right|^2 \tag{41}$$

where $\rho(\varepsilon_n)$ is the number of states per unit energy, the so called "density of states." Let's suppose that $\left| \left\langle n \left| \hat{\mathrm{V}} \right| i \right\rangle \right|$ doesn't change much over the ROI so we can take it outside the integrand.

$$\sum_{n\in \text{ ROI}} \mathbb{P}[i \to n; t] = \left| \left\langle n \left| \hat{\mathrm{V}} \right| i \right\rangle \right|^2 \int_{\text{ROI}} \mathrm{d}\varepsilon_n \rho(\varepsilon_n) \left(\frac{2\sin\left(\frac{\varepsilon_n - \varepsilon_i}{2} t\right)}{\varepsilon_n - \varepsilon_i} \right)^2 \tag{42}$$

So now as t becomes larger, the central bump falls ($\propto \frac{1}{t}$) entirely within the ROI, and then the density of states can be taken effectively constant over the sharply peaked integrand. Thus we can also take $\rho(\varepsilon_n)$ outside the integrand:

$$\sum_{n\in \text{ ROI}} \mathbb{P}[i\to n;t] = \left|\left\langle n\left|\hat{\mathrm{V}}\right|i\right\rangle\right|^2 \Big[\rho(\varepsilon_n)\Big|_{\varepsilon_i} \int_{\text{ROI}} \mathrm{d}\varepsilon_n \left(\frac{2\sin\left(\frac{\varepsilon_n-\varepsilon_i}{2}t\right)}{\varepsilon_n-\varepsilon_i}\right)^2 \tag{43}$$

So want:

$$\int_{\mathbb{R}} \mathrm{d}x \left(\frac{2\sin\left(\frac{\varepsilon_n-\varepsilon_i}{2}t\right)}{\varepsilon_n-\varepsilon_i}\right)^2 = t^2\frac{2}{t}\int_{\mathbb{R}} \mathrm{d}z \frac{\sin(z)^2}{z^2} \tag{44}$$

where

$$z=(x-y)t/2 \quad ; \quad \mathrm{d}z = t/2\mathrm{d}x \tag{45}$$

$$\Rightarrow 2t\int_{\mathbb{R}} \mathrm{sinc}(x)^2\mathrm{d}x \tag{46}$$

With an appropriate change of variables

$$\int_{\mathbb{R}} \mathrm{d}x \left(\frac{2\sin\left(\frac{\varepsilon_n-\varepsilon_i}{2}t\right)}{\varepsilon_n-\varepsilon_i}\right)^2 = \tau t \tag{47}$$

hence

Theorem 7.2:5 (Fermi's Golden Rule)

$$\sum_{n\in \text{ ROI}} \mathbb{P}[i\to n;t] \approx \Gamma t \tag{48}$$

where the transition rate, γ is:

$$\Gamma = \tau\left|\left\langle n\left|\hat{\mathrm{V}}\right|i\right\rangle\right|^2 \Big[\rho(\varepsilon_n)\Big|_{\varepsilon_n=\varepsilon_i} \tag{49}$$

This is not valid when: