

Fermi's Golden Rules

What is the most important equation in quantum mechanics?

According to David Griffiths it is:

$$E_n^{(1)} = \langle n | H_1 | n \rangle$$

“This is the fundamental result of first-order perturbation theory, as a *practical* matter it may well be the most important equation in quantum mechanics. It says that the first-order correction to the energy is the *expectation value* of the perturbation in the *unperturbed* state.”

But that describes quantum *statics*, and quantum *dynamics* is where it is at!

As Chalmers Sherwin puts it:

“Up to now, all the quantitative calculations have been concerned with the Hamiltonian functions which are independent of time—and therefore with Hamiltonian operators, H , which are independent of time. In a real sense, however, all that we have done so far is a mathematical exercise, because when the Hamiltonian is time-independent, **nothing observable ever happens.**”

“It may come as something of a shock to discover, after nine chapters, that we have yet to get down to the business of predicting experiments in a realistic, logically consistent way.”

So to my mind, the most important practical equations in quantum mechanics are Fermi's Two Golden Rules.

Fermi's First Golden Rule is

$$R = \frac{2\pi}{\hbar} \sum_c \frac{|\langle f | H_1 | c \rangle \langle c | H_1 | i \rangle|^2}{(E_i - E_c)^2} \rho(E)$$

provided there are no direct transitions from i to f

Fermi's First Golden Rule describes scattering.

Fermi's Second Golden Rule is

$$R = \frac{2\pi}{\hbar} |\langle f | H_1 | i \rangle|^2 \rho(E)$$

Fermi's Second Golden Rule describes absorption and stimulated emission.

R is the transition probability per second from $|i\rangle$ to $|f\rangle$

$|i\rangle$ is the initial state

$|f\rangle$ is the final state

$|c\rangle$ is an intermediate state

$\rho(E)$ is the final density of states

TIPT

FIRST QUANTIZED NRQM

FIRST QUANTIZATION: MATTER FIELDS ELECTRONS

SECOND QUANTIZATION: RADIATION FIELDS PHOTONS

FIRST QUANTIZATION $\Rightarrow \vec{E}, \vec{B} \quad (\psi, \vec{A})$

NR $\Rightarrow E = KE + PE$

$$H = \frac{p^2}{2m} + V(x) \quad (\psi, \vec{A})$$

$$E^2 = p^2 c^2 + m_0^2 c^4$$

HYDROGEN

$|m, l, m\rangle$

$E_m \quad m^2 \text{ degeneracy}$

LEFT OUT: MAGNETIC INTERACTIONS

SPIN ELECTRON MAGNETIC MOMENT

SPIN PROTON " "

MAGNETIC MOMENT DUE TO ORBIT

$$H = -\vec{\mu} \cdot \vec{B} \quad \text{ZEEMAN EFFECT}$$

$$H = -\vec{p} \cdot \vec{E} \quad \text{STARK EFFECT}$$

$$H = \gamma \vec{L} \cdot \vec{S} \quad \text{SPIN-ORBIT INTERACTION}$$

$$H = \beta \vec{S}_1 \cdot \vec{S}_2 \quad \text{SPIN-SPIN INTERACTION}$$

THE ABOVE ARE
CORRECTIONS TO POTENTIAL ENERGY

TWO CORRECTIONS TO KINETIC ENERGY

(1) REDUCED MASS $\frac{p^2}{2\mu}$

(2) MASS INCREASE

FINE STRUCTURE

$$H_{FS} = H_R + H_{LS} + H_D$$

RELATIVITY SPIN-ORBIT DARWIN

HYPERFINE STRUCTURE

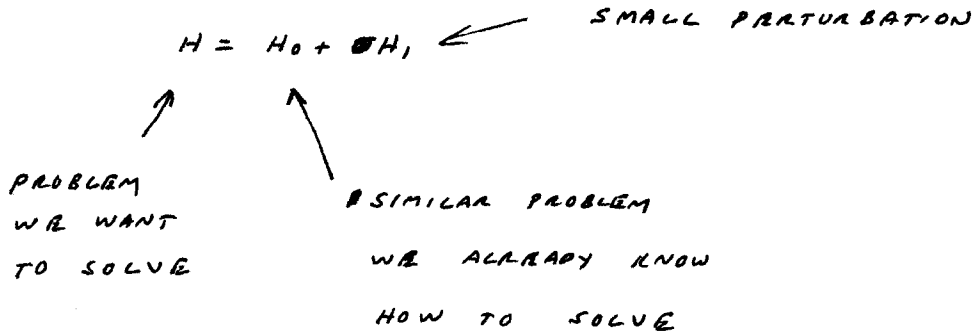
$$H_{HF} = \beta \vec{S}_1 \cdot \vec{S}_2$$

ZEEMAN EFFECT

STARK EFFECT

LECTURE TIME-INDEPENDENT PERTURBATION THEORY (TIPT)

PHILOSOPHY: BREAK TI HAMILTONIAN INTO TWO PIECES



$$H |m'\rangle = E_m' |m'\rangle$$

TIPT gives us approx solutions to $H |\psi_m\rangle = E_m |\psi_m\rangle$

in terms of $H_0 |\psi_m^0\rangle = E_m^0 |\psi_m^0\rangle$.

$$H_0 |m\rangle = E_m |m\rangle$$

We want to find the e_v and e_v' of H ,

\downarrow
 E_m'

\downarrow

$|m'\rangle$

in terms of the e_v and e_v' of H_0 .

\downarrow
 E_m

\downarrow

$|m\rangle$

TIPT is also often called "STATIONARY STATE
PERTURBATION THEORY"
or
"STATIONARY PERTURBATION
THEORY"

PHILOSOPHY OF THE SOLUTION

$$H = H_0 + \lambda H_1$$

- 1) as $\lambda \rightarrow 0$ we must ~~return to the~~ ^{return to the} ~~the~~ H_0 ~~to~~ eV and $e\vec{v}$ of H_0
- 2) often this happens smoothly, and in these cases TIPT is a good way to solve the problem.

WARNING! Sometimes this does not happen!

EXAMPLE: Cooper pairs ... bound states out of free states

$\Rightarrow +V$ only slightly different than $-V$

but this is absurd since $-V \Rightarrow$ bound

$+V \Rightarrow$ stay free.

MORAL: Some important problems are too hard for perturbation theory. No small parameter to expand in.

- 3) make a power series in λ ; ~~not~~ want result independent of the value of λ ; ~~not~~ ^{deduce} ~~not~~ ~~to~~ ~~be~~ coeffs of the same power of λ must vanish.

METHOD:

E. SCHRÖDINGER ANN PHYSIK 90, 437 (1926)

$$H = H_0 + \lambda H_1$$

FIRST ORDER CORRECTION TO THE UNPERTURBED WAVEFUNCTION

SECOND ORDER CORRECTION

$$|\psi_m\rangle = |\psi_m^0\rangle + \lambda |\psi_m^1\rangle + \lambda^2 |\psi_m^2\rangle + \dots$$

$$E_m = E_m^0 + \lambda E_m^1 + \lambda^2 E_m^2 + \dots$$

\uparrow \uparrow
 FIRST SECOND
 ORDER ORDER
 CORRECTION CORRECTION
 TO THE TO THE
 UNPERTURBED UNPERTURBED
 ENERGY

PUT THESE THREE LINES INTO THE TISE:

$$H |\psi_m\rangle = E_m |\psi_m\rangle \quad H |m'\rangle = E_m' |m'\rangle$$

ENERGY CORRECTIONS

$$E_m^I = E_m^{(0)} + E_m^{(1)} + E_m^{(2)} + E_m^{(3)} + \dots$$

ZEROth ORDER

$$E_m^{(0)} = E_m$$

H_1
APPEARS
0 TIMES

FIRST ORDER

$$E_m^{(1)} = \langle m | H_1 | m \rangle$$

1 TIME

SECOND ORDER

$$E_m^{(2)} = \sum_l' \frac{\langle m | H_1 | l \rangle \langle l | H_1 | m \rangle}{E_m - E_l}$$

2 TIMES

THIRD ORDER

$$E_m^{(3)} = \sum_l' \sum_k' \frac{\langle m | H_1 | l \rangle \langle l | H_1 | k \rangle \langle k | H_1 | m \rangle}{(E_m - E_k)(E_m - E_l)}$$

$$- \sum_l' \frac{\langle m | H_1 | l \rangle \langle l | H_1 | m \rangle \langle m | H_1 | m \rangle}{(E_m - E_l)^2}$$

WAVEFN CORRECTIONS

$$|m'\rangle = |m^{(0)}\rangle + |m^{(1)}\rangle + |m^{(2)}\rangle + \dots$$

ZEROth ORDER $|m^{(0)}\rangle = |m\rangle$

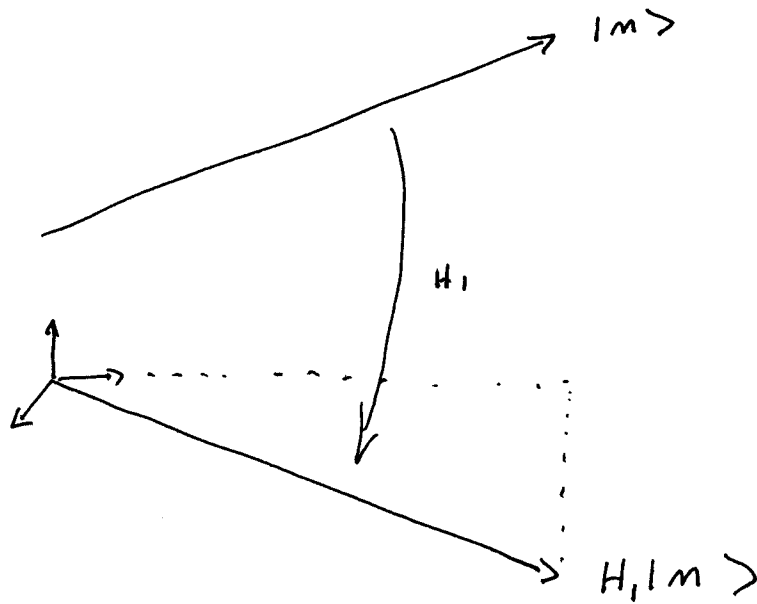
FIRST ORDER $|m^{(1)}\rangle = \sum_L' |L\rangle \frac{\langle L | H_1 | m \rangle}{(E_m - E_L)}$

SECOND ORDER $\frac{|L\rangle \langle L|}{(E_m - E_L)} H_1 |m\rangle$

$$|m^{(2)}\rangle = \sum_L' \sum_K' \frac{|L\rangle \langle L|}{(E_m - E_L)} H_1 \frac{|K\rangle \langle K|}{(E_m - E_K)} H_1 |m\rangle$$

$$- \frac{\langle m | H_1 | m \rangle}{(E_m - E_L)} \sum_L' \frac{|L\rangle \langle L|}{(E_m - E_L)} H_1 |m\rangle$$

GEOMETRY



FOC: PROJECT $H_1|m\rangle$ ONTO ALL OTHER BASIS VECTORS; WEIGHT BY ENERGY DIFFERENCES; SUM

SOC: PROJECT $H_1|m\rangle$ ONTO ALL OTHER BASIS VECTORS TWICE; WEIGHT EACH BY ENERGY DIFFS; SUM;

CORRECTION TO SOC DUE TO
SUBTRACT OFF A FIRST-ORDER ENERGY CORRECTIONS

SOME
MORE FINE PRINT

1) OUR EQUATIONS ONLY WORK IF STATES
ARE NOT DEGENERATE ...

\Rightarrow WE'LL ALSO NEED DEGTIPT

2) TIPT often gives very good e_n 's

3) TIPT often gives ~~poor~~ poor e_n 's

4) energy shift iff $\langle m | H_1 | m \rangle \neq 0$

H_1 must connect the states

The bigger the overlap, the bigger the shift.

5) Strong mixing for states close in energy

Weak mixing for states distant in energy.

The TIPT results for the energy corrections are given by:

$$E'_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + E_n^{(3)} + \dots$$

where

$$E_n^{(1)} = \langle n | \mathcal{H}_1 | n \rangle$$

$$E_n^{(2)} = \sum_1' \frac{\langle n | \mathcal{H}_1 | l \rangle \langle l | \mathcal{H}_1 | n \rangle}{E_n - E_l}$$

$$E_n^{(3)} = \sum_1' \sum_k' \frac{\langle n | \mathcal{H}_1 | l \rangle \langle l | \mathcal{H}_1 | k \rangle \langle k | \mathcal{H}_1 | n \rangle}{(E_n - E_l)(E_n - E_k)} - \sum_1' \frac{\langle n | \mathcal{H}_1 | l \rangle \langle l | \mathcal{H}_1 | n \rangle \langle n | \mathcal{H}_1 | n \rangle}{(E_n - E_l)^2}$$

And the TIPT results for the wavefunction corrections are given by:

$$|n'\rangle = |n^{(0)}\rangle + |n^{(1)}\rangle + |n^{(2)}\rangle + \dots$$

where

$$|n^{(1)}\rangle = \sum_1' \frac{|l\rangle \langle l|}{E_n - E_l} \mathcal{H}_1 |n\rangle$$

$$|n^{(2)}\rangle = \sum_1' \sum_k' \frac{|l\rangle \langle l|}{E_n - E_l} \mathcal{H}_1 \frac{|k\rangle \langle k|}{E_n - E_k} \mathcal{H}_1 |n\rangle - \frac{\langle n | \mathcal{H}_1 | n \rangle}{E_n - E_l} \sum_1' \frac{|l\rangle \langle l|}{E_n - E_l} \mathcal{H}_1 |n\rangle$$

Notice that the perturbation Hamiltonian \mathcal{H}_1 appears in each correction term a total of m-times where m is the order of the correction.

Chapter 15

Time-Independent Perturbation Theory (TIPT)

Time-independent perturbation theory (TIPT) is an approximation method used for systems which have small variations from systems we can solve or have already solved. It often gives good eigenvalues but less accurate eigenvectors.

The strategy is to split the Hamiltonian into two pieces, *i.e.*,

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 \tag{1}$$

where \mathcal{H} is the Hamiltonian of the problem we want to solve, \mathcal{H}_0 is the soluable Hamiltonian, and \mathcal{H}_1 is the deviation from the soluable Hamiltonian. For instance, we know the solution for an infinite square well. We can treat an infinite square well with a "brick" in the middle as a combination of the infinite square well and the brick.

Since there is no dependence on time, TIPT necessarily addresses only stationary states. It is thus also known as stationary state perturbation theory or stationary perturbation theory. It is occasionally known as Rayleigh-Schrodinger perturbation theory¹.

Non-Degenerate TIPT

TIPT gives approximate solutions to the TISE

$$\mathcal{H}|\psi_n\rangle = E_n|\psi_n\rangle$$

in terms of a reference TISE

$$\mathcal{H}_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle,$$

where superscripts in parenthesis indicate the order of the correction. The unperturbed system is the zeroth order approximation, so the above equation describes an unperturbed system. We can adjust the zeroth order approximation by adding a first order correction, which we can further adjust by adding a second order correction, and so on until the desired degree of precision is attained, *i.e.*,

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \dots \tag{3}$$

It is traditional to write equation (1)

$$\mathcal{H} = \mathcal{H}_0 + \lambda\mathcal{H}_1 \tag{2}$$

¹ Sakurai, *Modern Quantum Mechanics* (Addison-Wesley Publishing Company, Reading, Massachusetts, 1994), revised ed., p. 285.

where λ is a constant that can be varied. Then as $\lambda \rightarrow 0$, $\mathcal{H} \rightarrow \mathcal{H}_0$, and the TISE returns the eigenvalues and eigenvectors of the unperturbed problem. When this happens smoothly, TIPT is a good approach. On occasion, there is a discontinuity in the wave function which is reflected by a discontinuity as $\lambda \rightarrow 0$, and TIPT does not work.

Superconductivity is one such phenomena. A significant portion of the reason that superconductivity resisted explanation for decades is that a perturbative approach, which was attempted repeatedly, does not apply. The formation of two bound electrons in a Cooper pair from two free electrons is discontinuous.

Given that the wave function is continuous, we will form a power series in λ , and deduce results independent of λ by using the fact that the coefficients of similar powers of λ must be equal. This method was first published by Schrodinger in 1926.

For

$$\mathcal{H} = \mathcal{H}_0 + \lambda\mathcal{H}_1,$$

the eigenenergies and eigenfunctions can be written,

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots, \quad (4)$$

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \dots. \quad (5)$$

Notice equations (3) and (4) are the same if $\lambda = 1$, and that is how equation (3) is justified, as is the analogous equation for the wave function. Substituting all three of the above equations in the TISE,

$$\begin{aligned} \mathcal{H}|\psi_n\rangle &= E_n|\psi_n\rangle \\ \Rightarrow (\mathcal{H}_0 + \lambda\mathcal{H}_1) \left(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \dots \right) \\ &= \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \right) \left(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \dots \right) \\ \Rightarrow \mathcal{H}_0|\psi_n^{(0)}\rangle + \lambda\mathcal{H}_0|\psi_n^{(1)}\rangle + \lambda^2\mathcal{H}_0|\psi_n^{(2)}\rangle + \dots \\ &\quad + \lambda\mathcal{H}_1|\psi_n^{(0)}\rangle + \lambda^2\mathcal{H}_1|\psi_n^{(1)}\rangle + \lambda^3\mathcal{H}_1|\psi_n^{(2)}\rangle + \dots \\ &= E_n^{(0)}|\psi_n^{(0)}\rangle + \lambda E_n^{(0)}|\psi_n^{(1)}\rangle + \lambda^2 E_n^{(0)}|\psi_n^{(2)}\rangle + \dots \\ &\quad + \lambda E_n^{(1)}|\psi_n^{(0)}\rangle + \lambda^2 E_n^{(1)}|\psi_n^{(1)}\rangle + \lambda^3 E_n^{(1)}|\psi_n^{(2)}\rangle + \dots \\ &\quad + \lambda^2 E_n^{(2)}|\psi_n^{(0)}\rangle + \lambda^3 E_n^{(2)}|\psi_n^{(1)}\rangle + \lambda^4 E_n^{(2)}|\psi_n^{(2)}\rangle + \dots \quad (6) \end{aligned}$$

Other than a trivial solution, the only way for equation (6) to be true is that terms with the same power of λ are equal, *i.e.*,

$$\begin{aligned} \mathcal{H}_0|\psi_n^{(0)}\rangle &= E_n^{(0)}|\psi_n^{(0)}\rangle \\ \lambda\mathcal{H}_0|\psi_n^{(1)}\rangle + \lambda\mathcal{H}_1|\psi_n^{(0)}\rangle &= \lambda E_n^{(0)}|\psi_n^{(1)}\rangle + \lambda E_n^{(1)}|\psi_n^{(0)}\rangle \\ \lambda^2\mathcal{H}_0|\psi_n^{(2)}\rangle + \lambda^2\mathcal{H}_1|\psi_n^{(1)}\rangle &= \lambda^2 E_n^{(0)}|\psi_n^{(2)}\rangle + \lambda^2 E_n^{(1)}|\psi_n^{(1)}\rangle + \lambda^2 E_n^{(2)}|\psi_n^{(0)}\rangle \\ \lambda^3\mathcal{H}_0|\psi_n^{(3)}\rangle + \lambda^3\mathcal{H}_1|\psi_n^{(2)}\rangle &= \lambda^3 E_n^{(0)}|\psi_n^{(3)}\rangle + \lambda^3 E_n^{(1)}|\psi_n^{(2)}\rangle + \lambda^3 E_n^{(2)}|\psi_n^{(1)}\rangle + \lambda^3 E_n^{(3)}|\psi_n^{(0)}\rangle \end{aligned}$$

Dividing each equation by the appropriate power of λ ,

$$\mathcal{H}_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle \quad (7)$$

$$\mathcal{H}_0|\psi_n^{(1)}\rangle + \mathcal{H}_1|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}|\psi_n^{(0)}\rangle \quad (8)$$

$$\mathcal{H}_0|\psi_n^{(2)}\rangle + \mathcal{H}_1|\psi_n^{(1)}\rangle = E_n^{(0)}|\psi_n^{(2)}\rangle + E_n^{(1)}|\psi_n^{(1)}\rangle + E_n^{(2)}|\psi_n^{(0)}\rangle \quad (9)$$

$$\mathcal{H}_0|\psi_n^{(3)}\rangle + \mathcal{H}_1|\psi_n^{(2)}\rangle = E_n^{(0)}|\psi_n^{(3)}\rangle + E_n^{(1)}|\psi_n^{(2)}\rangle + E_n^{(2)}|\psi_n^{(1)}\rangle + E_n^{(3)}|\psi_n^{(0)}\rangle \quad (10)$$

which are independent of λ as desired. The eigenvalues and eigenvectors for equation (7) are zeroth order; they are the eigenvalues and eigenvectors of the unperturbed system. The eigenvalues and eigenvectors of equation (8), the equation formerly linear in λ , yield the first order corrections. Equation (9), formerly quadratic in λ , yields second order corrections; equation (10), formerly cubic in λ , yields third order corrections, and you can go to the order correction you want. First order corrections generally dominate, so we will do that explicitly, illustrating the general procedure.

Forming the inner product of $\langle\psi_n^{(0)}|$ with both sides of equation (8),

$$\langle\psi_n^{(0)}|\mathcal{H}_0|\psi_n^{(1)}\rangle + \langle\psi_n^{(0)}|\mathcal{H}_1|\psi_n^{(0)}\rangle = \langle\psi_n^{(0)}|E_n^{(0)}|\psi_n^{(1)}\rangle + \langle\psi_n^{(0)}|E_n^{(1)}|\psi_n^{(0)}\rangle \quad (11)$$

$$\Rightarrow \langle\psi_n^{(0)}|E_n^{(0)}|\psi_n^{(1)}\rangle + \langle\psi_n^{(0)}|\mathcal{H}_1|\psi_n^{(0)}\rangle = \langle\psi_n^{(0)}|E_n^{(0)}|\psi_n^{(1)}\rangle + \langle\psi_n^{(0)}|E_n^{(1)}|\psi_n^{(0)}\rangle \quad (12)$$

$$\Rightarrow \langle\psi_n^{(0)}|\mathcal{H}_1|\psi_n^{(0)}\rangle = E_n^{(1)}\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle \quad (13)$$

$$\Rightarrow E_n^{(1)} = \langle\psi_n^{(0)}|\mathcal{H}_1|\psi_n^{(0)}\rangle$$

is the first order correction to the eigenenergy. Now, in equation (11), we let the Hermitian Hamiltonian \mathcal{H}_0 act to the left which resulted in the eigenvalue $E_n^{(0)}$ being in the first bracket in equation (12). The first brackets on both sides of the equation are then equal, so we subtract both of them resulting in equation (13). The eigenvalue $E_n^{(1)}$ on the right side of the equation is a constant so can be moved outside the bracket. The bracket that remains, $\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle$, is an inner product of identical states, *i.e.*, $\langle i|j\rangle = \delta_{ij}$, so is one, and we have an expression for the first order correction to the eigenenergy.

To attain the first order correction to the wave function, remember we can express $|\psi_n^{(1)}\rangle$ as a linear combination of any appropriate eigenstates. In this case, because we know $|\psi_n^{(0)}\rangle$, we can express the first order correction to the wave function as a linear combination of its eigenstates, *i.e.*,

$$|\psi_n^{(1)}\rangle = \sum_{m \neq n}^{\infty} a_m |\psi_m^{(0)}\rangle \quad (14)$$

where we have not included $a_n |\psi_n^{(0)}\rangle$ in the summation. This is because $|\psi_n^{(0)}\rangle$ is the zeroth order term for this particular wave function. In equation (5),

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

we see $|\psi_n^{(0)}\rangle$ as the first term on the right side of the equation so we do not include it as any portion of the first order correction. Similarly, the zeroth and first order corrections need to be excluded from the second order correction, and so on.

As previously indicated, equation (8) will yield first order corrections. Equation (8) is

$$\begin{aligned} \mathcal{H}_0|\psi_n^{(1)}\rangle + \mathcal{H}_1|\psi_n^{(0)}\rangle &= E_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}|\psi_n^{(0)}\rangle \\ \Rightarrow \left(\mathcal{H}_0 - E_n^{(0)}\right)|\psi_n^{(1)}\rangle &= -\left(\mathcal{H}_1 - E_n^{(1)}\right)|\psi_n^{(0)}\rangle. \end{aligned} \quad (15)$$

Substituting equation (14) into equation (15) yields

$$\left(\mathcal{H}_0 - E_n^{(0)}\right) \sum_{m \neq n}^{\infty} a_m |\psi_m^{(0)}\rangle = -\left(\mathcal{H}_1 - E_n^{(1)}\right) |\psi_n^{(0)}\rangle.$$

Forming an inner product with $\langle \psi_l^{(0)} |$,

$$\langle \psi_l^{(0)} | \left(\mathcal{H}_0 - E_n^{(0)}\right) \sum_{m \neq n}^{\infty} a_m |\psi_m^{(0)}\rangle = -\langle \psi_l^{(0)} | \left(\mathcal{H}_1 - E_n^{(1)}\right) |\psi_n^{(0)}\rangle \quad (16)$$

$$\begin{aligned} \Rightarrow \langle \psi_l^{(0)} | \mathcal{H}_0 \sum_{m \neq n}^{\infty} a_m |\psi_m^{(0)}\rangle - \langle \psi_l^{(0)} | E_n^{(0)} \sum_{m \neq n}^{\infty} a_m |\psi_m^{(0)}\rangle &= -\langle \psi_l^{(0)} | \mathcal{H}_1 |\psi_n^{(0)}\rangle + \langle \psi_l^{(0)} | E_n^{(1)} |\psi_n^{(0)}\rangle \\ \Rightarrow \langle \psi_l^{(0)} | E_l^{(0)} \sum_{m \neq n}^{\infty} a_m |\psi_m^{(0)}\rangle - \langle \psi_l^{(0)} | E_n^{(0)} \sum_{m \neq n}^{\infty} a_m |\psi_m^{(0)}\rangle &= -\langle \psi_l^{(0)} | \mathcal{H}_1 |\psi_n^{(0)}\rangle + \langle \psi_l^{(0)} | E_n^{(1)} |\psi_n^{(0)}\rangle \end{aligned}$$

where the Hermitian Hamiltonian has operated to the left in the first term. If $l = n$, the left side of the equation is the difference of two identical terms, so would be zero. We have already exploited that relationship to develop an expression for $E_n^{(1)}$. If $l \neq n$, the last equation can be written,

$$\begin{aligned} E_l^{(0)} \sum_{m \neq n}^{\infty} a_m \langle \psi_l^{(0)} | \psi_m^{(0)} \rangle - E_n^{(0)} \sum_{m \neq n}^{\infty} a_m \langle \psi_l^{(0)} | \psi_m^{(0)} \rangle &= -\langle \psi_l^{(0)} | \mathcal{H}_1 |\psi_n^{(0)}\rangle + E_n^{(1)} \langle \psi_l^{(0)} | \psi_n^{(0)} \rangle \\ \left(E_l^{(0)} - E_n^{(0)}\right) \sum_{m \neq n}^{\infty} a_m \langle \psi_l^{(0)} | \psi_m^{(0)} \rangle &= -\langle \psi_l^{(0)} | \mathcal{H}_1 |\psi_n^{(0)}\rangle + E_n^{(1)} \langle \psi_l^{(0)} | \psi_n^{(0)} \rangle \end{aligned}$$

Remembering $\langle i | j \rangle = \delta_{ij}$, so the left side of the equation is non-zero unless $l = m$. If $l = m$, the last term on the right is zero. Then

$$\begin{aligned} \left(E_m^{(0)} - E_n^{(0)}\right) a_m &= -\langle \psi_m^{(0)} | \mathcal{H}_1 |\psi_n^{(0)}\rangle \\ \Rightarrow a_m &= \frac{\langle \psi_m^{(0)} | \mathcal{H}_1 |\psi_n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}. \end{aligned} \quad (17)$$

Substituting this into equation (14) yields

$$|\psi_n^{(1)}\rangle = \sum_{m \neq n}^{\infty} \frac{\langle \psi_m^{(0)} | \mathcal{H}_1 |\psi_n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}} |\psi_m^{(0)}\rangle.$$

A common notation is to place a prime on the summation to denote $m \neq n$, and to leave the limit of the summation understood as ∞ , so the result is written

$$|\psi_n^{(1)}\rangle = \sum'_m \frac{\langle \psi_m^{(0)} | \mathcal{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} |\psi_m^{(0)}\rangle .$$

To find the second order correction for the energy, start with the equation formerly second order in λ , equation (9).

$$\mathcal{H}_0 |\psi_n^{(2)}\rangle + \mathcal{H}_1 |\psi_n^{(1)}\rangle = E_n^{(0)} |\psi_n^{(2)}\rangle + E_n^{(1)} |\psi_n^{(1)}\rangle + E_n^{(2)} |\psi_n^{(0)}\rangle \quad (9)$$

Forming the inner product with $\langle \psi_n^{(0)} |$

$$\begin{aligned} \langle \psi_n^{(0)} | \mathcal{H}_0 | \psi_n^{(2)} \rangle + \langle \psi_n^{(0)} | \mathcal{H}_1 | \psi_n^{(1)} \rangle \\ = \langle \psi_n^{(0)} | E_n^{(0)} | \psi_n^{(2)} \rangle + \langle \psi_n^{(0)} | E_n^{(1)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(0)} | E_n^{(2)} | \psi_n^{(0)} \rangle \end{aligned} \quad (18)$$

$$\begin{aligned} \Rightarrow \langle \psi_n^{(0)} | \cancel{E_n^{(0)}} | \psi_n^{(2)} \rangle + \langle \psi_n^{(0)} | \mathcal{H}_1 | \psi_n^{(1)} \rangle \\ = \langle \psi_n^{(0)} | \cancel{E_n^{(0)}} | \psi_n^{(2)} \rangle + E_n^{(1)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + E_n^{(2)} \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle \end{aligned} \quad (19)$$

$$\begin{aligned} \Rightarrow E_n^{(2)} &= \langle \psi_n^{(0)} | \mathcal{H}_1 | \psi_n^{(1)} \rangle \\ &= \langle \psi_n^{(0)} | \mathcal{H}_1 | \sum'_m \frac{\langle \psi_m^{(0)} | \mathcal{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} |\psi_m^{(0)}\rangle \\ &= \sum'_m \frac{\langle \psi_m^{(0)} | \mathcal{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \langle \psi_n^{(0)} | \mathcal{H}_1 | \psi_m^{(0)} \rangle \end{aligned} \quad (20)$$

$$\Rightarrow E_n^{(2)} = \sum'_m \frac{|\langle \psi_m^{(0)} | \mathcal{H}_1 | \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} .$$

In equation (18), the Hermitian \mathcal{H}_0 operated to the left resulting in the eigenvalue $E_n^{(0)}$ in the bracket. The first term on both sides of the equation are identical so are subtracted in equation (19). Also in (19), the constants in the last two terms are moved outside the brackets. Because of the orthonormality condition, $\langle i | j \rangle = \delta_{ij}$, $E_n^{(1)} \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = 0$ and $E_n^{(2)} \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle = E_n^{(2)}$. The two brackets in equation (20) are Hermitian adjuncts so have the same magnitude, so the second order correction is usually written in terms of the magnitude squared.

This process should look familiar to the calculations for first order corrections. The strategy for all higher order corrections is similar. You attain the desired order correction by addressing the equation formerly of that order in λ . You need the results from all lower order equations to

use in the desired solution. The \mathcal{H}_i can operate to the left or right because they are Hermitian. Constants can be removed from brackets, just like constants can be removed from integrals. The orthonormality relation, $\langle i|j\rangle = \delta_{ij}$, will apply to bras and kets which are adjacent. Calculations for higher order corrections will be longer because there are more terms to consider. Also, you need to exclude terms which are already included in lower order corrections.

Notation. Not everyone places parenthesis on superscripts to differentiate them from exponents, in which case you must discriminate that E_n^2 means second order correction and λ^2 means λ squared, for instance. Also, a common economy is to express a zeroth order bra or ket by its subscript only. These mean

$$E_n^{(0)} \rightarrow E_n, \quad E_n^{(1)} \rightarrow E_n^1, \quad \text{and} \quad |\psi_l^{(0)}\rangle \rightarrow |l\rangle,$$

so our results may be written

$$\begin{aligned} E_n^1 &= \langle n|\mathcal{H}_1|n\rangle \\ |\psi_n^1\rangle &= \sum'_m \frac{\langle m|\mathcal{H}_1|n\rangle}{E_n - E_m} |m\rangle \\ E_n^2 &= \sum'_m \frac{|\langle m|\mathcal{H}_1|n\rangle|^2}{E_n - E_m} \end{aligned}$$

Notice the perturbation Hamiltonian appears in all corrections, and a difference of eigenenergies appears in two of three. Taking advantage of these recurrences, notation is sometimes further shortened to

$$\langle m|\mathcal{H}_1|n\rangle \rightarrow \mathcal{H}'_{mn}, \quad \text{and} \quad E_n - E_m = \hbar\omega_{nm},$$

so in this notation our results appear as

$$\begin{aligned} E_n^1 &= \mathcal{H}'_{nn} \\ |\psi_n^1\rangle &= \sum'_m \frac{\mathcal{H}'_{mn}}{\hbar\omega_{nm}} |m\rangle \\ E_n^2 &= \sum'_m \frac{|\mathcal{H}'_{mn}|^2}{\hbar\omega_{nm}}. \end{aligned}$$

Corrections to energies are the primary application of TIPT, and on occasion, the first order corrections vanish so second order corrections are necessary to attain any amendment. Recognize that $|\psi_n^1\rangle$ and E_n^2 are infinite sums so may required some cleverness to calculate. The first order correction to the energy is dominantly the most useful of the above results.

Two additional caveats. Our development applies to an energy spectrum that is discrete and non-degenerate. If the spectrum is not discrete, continuum states need to be addressed and $\Sigma \rightarrow \int$. Also, if two states have the same energy, if the system is degenerate, the denominator

in both summations includes a term that would be zero, and we don't like that. We need another approach for a degenerate system.

An example application is an infinite square well with a brick of height V_0 as pictured at the right. If we use $x = 0$ and $x = L$ as the walls of the box, we can express all wave functions in terms of sines and

$$|\psi_n^{(0)}\rangle = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right),$$

$$E_n^{(0)} = n^2 \frac{\hbar^2 \pi^2}{2mL^2}, \quad \text{where } n = 1, 2, 3, \dots$$

The Hamiltonian for the unperturbed infinite square well is

$$\mathcal{H} = \frac{p^2}{2m} + V(x) = \frac{p^2}{2m}$$

if the bottom of the well is defined as $V(x) = 0$. We can write the Hamiltonian for the perturbed system as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 = \frac{p^2}{2m} + V(x) = \frac{p^2}{2m} + V_0$$

$$\text{RA } \mathcal{H}_0 = \frac{p^2}{2m}, \quad \text{and } \mathcal{H}_1 = V_0.$$

The first order correction to the energy is

$$\begin{aligned} E_n^1 &= \langle n | \mathcal{H}_1 | n \rangle \\ &= \left\langle \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \left| V(x) \right| \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \right\rangle \\ &= \frac{2}{L} \int_{-\infty}^{\infty} \left(\sin\left(\frac{n\pi x}{L}\right) \right)^* V_0 \sin\left(\frac{n\pi x}{L}\right) dx \\ &= \frac{2V_0}{L} \int_{L/2}^L \sin^2\left(\frac{n\pi x}{L}\right) dx \\ &= \frac{2V_0}{L} \left[\frac{1}{2}x - \frac{L}{4n\pi} \sin\left(\frac{2n\pi}{L}x\right) \right]_{L/2}^L \\ &= \frac{2V_0}{L} \left[\frac{1}{2} \left(L - \frac{L}{2} \right) - \frac{L}{4n\pi} \left(\sin(2n\pi) - \sin(n\pi) \right) \right] \end{aligned}$$

where both sine terms are zero for all n , so

$$E_n^1 = \frac{V_0}{L} \frac{L}{2} = \frac{V_0}{2}$$

$$\Rightarrow E_n = n^2 \frac{\hbar^2 \pi^2}{2mL^2} + \frac{V_0}{2},$$