

# 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 theory<sup>1</sup>.

### 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)

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

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

where  $\lambda$  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  $\lambda$ , and deduce results independent of  $\lambda$  by using the fact that the coefficients of similar powers of  $\lambda$  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  $\lambda$  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  $\lambda$ ,

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

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

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

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

which are independent of  $\lambda$  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  $\lambda$ , yield the first order corrections. Equation (9), formerly quadratic in  $\lambda$ , yields second order corrections; equation (10), formerly cubic in  $\lambda$ , 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  $\infty$ , 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  $\lambda$ , 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  $\lambda$ . 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  $\lambda^2$  means  $\lambda$  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.

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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

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

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

so the first order correction is like the "area of the perturbation" being spread evenly over the width of the well.

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### Degenerate TIPT

Two-fold degeneracy means two eigenenergies are identical. The Hamiltonian is diagonal in the energy basis. Two-fold degeneracy can occur anywhere in the matrix, and arbitrarily, we will represent the degeneracy at the lowest energy, so

$$\mathcal{H}_0 = \begin{pmatrix} E_0 & 0 & 0 & 0 & \cdots \\ 0 & E_0 & 0 & 0 & \cdots \\ 0 & 0 & E_1 & 0 & \cdots \\ 0 & 0 & 0 & E_2 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}.$$

Treat the non-degenerate states with non-degenerate TIPT. We need to use degenerate TIPT only on degenerate states. This not only simplifies the treatment of what is likely the bulkiest part of this problem, but it also allows us to address just the subspace containing the degeneracy to examine that portion of the problem. In the degenerate subspace,

$$\mathcal{H}_0 = \begin{pmatrix} E_0 & 0 \\ 0 & E_0 \end{pmatrix}, \quad \text{and} \quad |\psi_n^{(0)}\rangle = \begin{pmatrix} |\psi_a^{(0)}\rangle \\ |\psi_b^{(0)}\rangle \end{pmatrix},$$

where the subscripts  $a$  and  $b$  are used to denote distinctly different states. The eigenvalue equation in this subspace is

$$\begin{aligned} \mathcal{H}_0 \begin{pmatrix} |\psi_a^{(0)}\rangle \\ |\psi_b^{(0)}\rangle \end{pmatrix} &= \begin{pmatrix} E_0 & 0 \\ 0 & E_0 \end{pmatrix} \begin{pmatrix} |\psi_a^{(0)}\rangle \\ |\psi_b^{(0)}\rangle \end{pmatrix} \\ \Rightarrow \mathcal{H}_0 |\psi_a^{(0)}\rangle &= E_0 |\psi_a^{(0)}\rangle \quad \text{and} \quad \mathcal{H}_0 |\psi_b^{(0)}\rangle = E_0 |\psi_b^{(0)}\rangle. \end{aligned}$$

This is simply a statement of degeneracy. If degeneracy exists in unperturbed states, then any linear combination,

$$|\psi_n^{(0)}\rangle = \alpha |\psi_a^{(0)}\rangle + \beta |\psi_b^{(0)}\rangle$$

is an eigenstate of  $\mathcal{H}_0$ .

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To demonstrate the linear combination is an eigenstate,

$$\begin{aligned} \mathcal{H}_0 |\psi_n^{(0)}\rangle &= \mathcal{H}_0 [\alpha |\psi_a^{(0)}\rangle + \beta |\psi_b^{(0)}\rangle] \\ &= \alpha \mathcal{H}_0 |\psi_a^{(0)}\rangle + \beta \mathcal{H}_0 |\psi_b^{(0)}\rangle \\ &= \alpha E_0 |\psi_a^{(0)}\rangle + \beta E_0 |\psi_b^{(0)}\rangle \\ &= \alpha E_0 [\alpha |\psi_a^{(0)}\rangle + \beta |\psi_b^{(0)}\rangle] \\ \Rightarrow \mathcal{H}_0 |\psi_n^{(0)}\rangle &= E_0 |\psi_n^{(0)}\rangle, \end{aligned}$$

where the eigenvalue will be the appropriate eigenvalue which we have denoted as  $E_0$  consistent with our assumed Hamiltonian.

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Having established background and meaning of degeneracy, and the fact that a linear combination of degenerate states is an eigenstate, we return to equation (8),

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

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

$$\langle\psi_a^{(0)}|\mathcal{H}_0|\psi_n^{(1)}\rangle + \langle\psi_a^{(0)}|\mathcal{H}_1|\psi_n^{(0)}\rangle = \langle\psi_a^{(0)}|E_n^{(0)}|\psi_n^{(1)}\rangle + \langle\psi_a^{(0)}|E_n^{(1)}|\psi_n^{(0)}\rangle \quad (21)$$

$$\Rightarrow \langle\psi_a^{(0)}|E_n^{(0)}|\psi_n^{(1)}\rangle + \langle\psi_a^{(0)}|\mathcal{H}_1|\psi_n^{(0)}\rangle = \langle\psi_a^{(0)}|E_n^{(0)}|\psi_n^{(1)}\rangle + \langle\psi_a^{(0)}|E_n^{(1)}|\psi_n^{(0)}\rangle \quad (22)$$

$$\Rightarrow \langle\psi_a^{(0)}|\mathcal{H}_1\left(\alpha|\psi_a^{(0)}\rangle + \beta|\psi_b^{(0)}\rangle\right) = E_n^{(1)}\langle\psi_a^{(0)}\left(\alpha|\psi_a^{(0)}\rangle + \beta|\psi_b^{(0)}\rangle\right) \quad (23)$$

$$\Rightarrow \alpha\langle\psi_a^{(0)}|\mathcal{H}_1|\psi_a^{(0)}\rangle + \beta\langle\psi_a^{(0)}|\mathcal{H}_1|\psi_b^{(0)}\rangle = \alpha E_n^{(1)}\langle\psi_a^{(0)}|\psi_a^{(0)}\rangle + \beta E_n^{(1)}\langle\psi_a^{(0)}|\psi_b^{(0)}\rangle \quad (24)$$

$$\Rightarrow \alpha\langle\psi_a^{(0)}|\mathcal{H}_1|\psi_a^{(0)}\rangle + \beta\langle\psi_a^{(0)}|\mathcal{H}_1|\psi_b^{(0)}\rangle = \alpha E_n^{(1)} \quad (25)$$

$$\Rightarrow \alpha E_n^1 = \alpha\mathcal{H}'_{aa} + \beta\mathcal{H}'_{ab} \quad (26)$$

in the compact notation. In equation (21), the Hamiltonian acts to the left resulting in the eigenvalue being in the first bracket. The first term on both sides of the equation are identical so are subtracted in equation (22). A linear combination is substituted in equation (23), is distributed in equation (24) where the orthonormality condition is applied, resulting in equation (25). When the inner product of equation (8) and  $\langle\psi_b^{(0)}|$ , is formed,

$$\begin{aligned} \alpha\langle\psi_b^{(0)}|\mathcal{H}_1|\psi_a^{(0)}\rangle + \beta\langle\psi_b^{(0)}|\mathcal{H}_1|\psi_b^{(0)}\rangle &= \beta E_n^{(1)} \\ \Rightarrow \beta E_n^1 &= \alpha\mathcal{H}'_{ba} + \beta\mathcal{H}'_{bb} \end{aligned} \quad (27)$$

results in a parallel development. Solving equation (27) for  $\beta$ ,

$$\beta = \frac{\alpha\mathcal{H}'_{ba}}{E_n^1 - \mathcal{H}'_{bb}},$$

and substituting this into equation (26),

$$\begin{aligned} \alpha E_n^1 &= \alpha\mathcal{H}'_{aa} + \frac{\alpha\mathcal{H}'_{ba}}{E_n^1 - \mathcal{H}'_{bb}}\mathcal{H}'_{ab} \\ \Rightarrow \alpha\left(E_n^1 - \mathcal{H}'_{aa}\right)\left(E_n^1 - \mathcal{H}'_{bb}\right) &= \alpha\mathcal{H}'_{ba}\mathcal{H}'_{ab} \\ \Rightarrow \left(E_n^1\right)^2 - E_n^1\left(\mathcal{H}'_{aa} + \mathcal{H}'_{bb}\right) + \mathcal{H}'_{aa}\mathcal{H}'_{bb} - \mathcal{H}'_{ba}\mathcal{H}'_{ab} &= 0 \end{aligned}$$

which is quadratic in  $E_n^1$ . Using the quadratic formula

$$\begin{aligned} E_{n\pm}^1 &= \frac{1}{2}\left(\mathcal{H}'_{aa} + \mathcal{H}'_{bb} \pm \sqrt{(\mathcal{H}'_{aa} + \mathcal{H}'_{bb})^2 - 4(\mathcal{H}'_{aa}\mathcal{H}'_{bb} - \mathcal{H}'_{ba}\mathcal{H}'_{ab})}\right) \\ &= \frac{1}{2}\left(\mathcal{H}'_{aa} + \mathcal{H}'_{bb} \pm \sqrt{(\mathcal{H}'_{aa})^2 + 2\mathcal{H}'_{aa}\mathcal{H}'_{bb} + (\mathcal{H}'_{bb})^2 - 4\mathcal{H}'_{aa}\mathcal{H}'_{bb} + 4\mathcal{H}'_{ba}\mathcal{H}'_{ab}}\right) \\ &= \frac{1}{2}\left(\mathcal{H}'_{aa} + \mathcal{H}'_{bb} \pm \sqrt{(\mathcal{H}'_{aa})^2 - 2\mathcal{H}'_{aa}\mathcal{H}'_{bb} + (\mathcal{H}'_{bb})^2 + 4\mathcal{H}'_{ba}\mathcal{H}'_{ab}}\right) \end{aligned}$$

and since  $\mathcal{H}'_{ba} = (\mathcal{H}'_{ab})^*$ ,

$$E_{n\pm}^1 = \frac{1}{2} \left( \mathcal{H}'_{aa} + \mathcal{H}'_{bb} \pm \sqrt{(\mathcal{H}'_{aa} - \mathcal{H}'_{bb})^2 - 4|\mathcal{H}'_{ab}|^2} \right)$$

for a two-fold degeneracy.

### The Fine Structure of Hydrogen

A prominent application of TITP is explaining the minute splitting of the principal lines of the hydrogen spectrum. This splitting is known as the **fine structure of hydrogen**. The spectrum is the record of photons emitted or absorbed during electronic transitions between different quantum energy states.

Fine structure is explained by a combination of a relativistic correction, *i.e.* the orbital momentum of the electron  $p \neq \sqrt{2mE}$ , and a magnetic coupling correction. **Spin-orbit coupling** is the magnetic effect from the spin magnetic moment of the electron in the magnetic field of the proton caused by relative motion. Magnetic coupling dominated by an external magnetic field is known as **Zeeman effect**. The Hamiltonian

$$\mathcal{H} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

explains the principal spectrum but not the fine structure. The strategy is to treat this as  $\mathcal{H}_0$  and treat the relativistic and magnetic coupling corrections as perturbations, *i.e.*,

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 = \mathcal{H}_0 + (\mathcal{H}_{\text{rel}} + \mathcal{H}_{\text{so}})$$

where  $\mathcal{H}_{\text{rel}}$  describes the perturbation due to relativistic effects and  $\mathcal{H}_{\text{so}}$  describes the perturbation due to spin-orbit coupling, for instance.

Detailed development of these phenomena is available in many volumes including Griffiths, pp 235 – 244, Gasiorowicz, pp 271 – 282, Sakurai, pp 304 – 311, Cohen-Tannoudji, chapter 12, Shankar, pp 466 – 471, and numerous others. We will present only pertinent results.

The relativistic correction/energy shift is given by

$$E_{\text{rel}}^{(1)} = \frac{E_n^2}{2mc^2} \left( 3 - \frac{4n}{l + 1/2} \right). \quad (28)$$

Magnetic coupling yields an energy shift is modelled as  $\mathcal{H}_{\text{mag}} = -\vec{\mu} \cdot \vec{B}$  from classical theory. The spin-orbit correction/energy shift is

$$E_{\text{so}}^{(1)} = \frac{E_n^2}{mc^2} \left( \frac{n[j(j+1) - l(l+1) - 3/4]}{l(l+1/2)(l+1)} \right) \quad (29)$$

where  $\vec{J} = \vec{L} + \vec{S}$  and addition of angular momentum states is a necessary consideration. Combining equations (28) and (29), we can calculate fine structure splitting using

$$E_{\text{fs}}^{(1)} = \frac{E_n^2}{2mc^2} \left( 3 - \frac{4n}{j + 1/2} \right).$$

If you want to derive this from equations (28) and (29), realize the intrinsic spin of an electron is  $1/2$ , so  $j = l \pm 1/2$  and the result is the boxed equation for both  $j = l + 1/2$  and  $j = l - 1/2$ .

The principal energy levels of hydrogen are

$$E_n = - \left[ \frac{m}{2\hbar} \left( \frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{n^2} \right] = - \frac{13.6eV}{n^2} = - \frac{mc^2\alpha^2}{2n^2}$$

in terms of the **fine structure constant**

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137}.$$

This is the uncorrected energy, so the energy including both the relativistic and spin-orbit corrections is

$$\begin{aligned} E_n + E_{\text{fs}}^{(1)} &= -\frac{mc^2\alpha^2}{2n^2} + \left( \frac{mc^2\alpha^2}{2n^2} \right)^2 \frac{1}{2mc^2} \left( 3 - \frac{4n}{j+1/2} \right) \\ &= -\frac{mc^2\alpha^2}{2n^2} \left[ 1 + \frac{mc^2\alpha^2}{2n^2} \frac{1}{2mc^2} \left( \frac{4n}{j+1/2} - 3 \right) \right] \end{aligned}$$

$$\Rightarrow E_n + E_{\text{fs}}^{(1)} = -\frac{13.6eV}{n^2} \left[ 1 + \frac{\alpha^2}{n^2} \left( \frac{n}{j+1/2} - \frac{3}{4} \right) \right].$$

If an external magnetic field dominates, Zeeman effect,

$$\mathcal{H}_1 = -\vec{\mu} \cdot \vec{B} = -\frac{\mu_B}{\hbar} (\vec{L} + 2\vec{S}) \cdot \vec{B}$$

where  $\mu_B = \frac{e\hbar}{2m} = 5.788 \times 10^{-5} eV/T$

is a convenient constant known as the Bohr magneton. Including perturbative effects with energies

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 \Rightarrow E_n + \mu_B g_j B_{\text{ext}} m_j$$

where

$$g_j = \left[ 1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)} \right]$$

is known as the **Lande g-factor**. The Lande g-factor expresses the ratio of the total magnetic moment to the total angular momentum of the electron.