

Time-independent perturbation theory

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Outline

- 1 Outline
- 2 The set up
- 3 First order perturbation theory
- 4 Second order perturbation theory
- 5 Keywords and References

- 1 Outline
- 2 The set up
- 3 First order perturbation theory
- 4 Second order perturbation theory
- 5 Keywords and References

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- 1 Outline
- 2 The set up**
- 3 First order perturbation theory
- 4 Second order perturbation theory
- 5 Keywords and References

Perturbations

Solvable problems in quantum mechanics are rare: they always seem to involve special symmetries. So one has to look for methods of wider applicability.

Assume that we know the eigenvalues and eigenvectors of a Hamiltonian H_0 . Label them by $|E_i^0\rangle$, where $H_0 |E_i^0\rangle = E_i^0 |E_i^0\rangle$. Also let the eigenstates be normalized: $\langle E_i^0 | E_i^0 \rangle = 1$. Can we use this knowledge to find the eigensystem of a Hamiltonian $H = H_0 + \epsilon H_1$?

The simplest case is when $[H_1, H_0] = 0$. In that case, H_0 and H have the same eigenvectors. The perturbed energies are

$$E_i = E_i^0 + \epsilon \langle E_i^0 | H_1 | E_i^0 \rangle.$$

The one complication which may arise is if some of the eigenvalues of H_0 are degenerate. In this case, we may have to diagonalize small blocks within H_1 .

Zeeman effect: the hydrogen atom in a magnetic field

If we put a Hydrogen atom in an external magnetic field, \mathbf{B} , then this would add an extra term in the Hamiltonian of the form

$$H' = \frac{e}{2m} \mathbf{L} \cdot \mathbf{B}.$$

Clearly, this gives rise to the **Lorentz force** on the electron. Any externally applied constant field would also be homogeneous on the length scale of an atom, so we will treat \mathbf{B} as constant. Taking $\hat{\mathbf{B}}$ to be the direction of quantization, we find $H' = \omega L_z$, where $\omega = eB/2m$ is the **cyclotron frequency**.

If we define $\vec{\mu}$, the **magnetic moment** of the electron, by writing

$$H' = -\vec{\mu} \cdot B,$$

then $\vec{\mu} = \mu_B \mathbf{L}$, where the **Bohr magneton**, $\mu_B = e/(2m)$, is the natural unit of magnetic moments. Generally $\gamma = q/(2M)$ is called the **gyromagnetic ratio** of a particle of charge q and mass M .

Problem 14.1: Zeeman splitting

There is a large degeneracy of the states $|nlms\rangle$ in a **hydrogenic atom**, part of which can be easily lifted by applying a magnetic field. Knowing that $\mu_B = 9.2741 \times 10^{-24}$ Joules/Tesla, $e^2 = 1/137.036$, and $e = 0.511$ MeV, find the conversion from Tesla to GeV.

Next check whether or not the effect of a 1 Tesla field applied in a lab can be treated in perturbation theory. **Magnetars** are neutron stars with surface magnetic fields of 10^8 – 10^{11} Tesla. Could magnetic effects of atoms at the surface of these cold stars be considered in perturbation theory. Find the critical magnetic field B_0 at which the cyclotron frequency equals the Rydberg, and the perturbation can no longer be considered small.

Examine the shift in energy of a Coulomb state $|nlm\rangle$, assuming that the direction $\hat{\mathbf{B}}$ defines the z-axis.

Series solution

In the more general case, it may be useful to assume that the energies of the perturbed Hamiltonian have a Taylor expansion in ϵ . In this case we write

$$\begin{aligned} E_i &= E_i^0 + \epsilon E_i^1 + \epsilon^2 E_i^2 + \dots, \\ |E_i\rangle &= |E_i^0\rangle + \epsilon |E_i^1\rangle + \epsilon^2 |E_i^2\rangle + \dots. \end{aligned}$$

Then the eigenvalue equation, $H |E_i\rangle = E_i |E_i\rangle$ can be written as the master equation

$$\begin{aligned} (H_0 + \epsilon H_1) (|E_i^0\rangle + \epsilon |E_i^1\rangle + \epsilon^2 |E_i^2\rangle + \dots) \\ = (E_i^0 + \epsilon E_i^1 + \epsilon^2 E_i^2 + \dots) (|E_i^0\rangle + \epsilon |E_i^1\rangle + \epsilon^2 |E_i^2\rangle + \dots) \end{aligned}$$

Since the equality holds for any value of ϵ , we can equate equal powers of ϵ . The leading term of the master equation is the eigenvalue equation of the unperturbed system.

A concrete example

Take

$$H_0 = \begin{pmatrix} 1 & 0 \\ 0 & 2 \end{pmatrix}, \quad H_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \text{so} \quad H(\epsilon) = \begin{pmatrix} 1 & \epsilon \\ \epsilon & 2 \end{pmatrix}.$$

The eigenvalues are $\lambda_{\pm} = (3 \pm D)/2$ where $D^2 = 1 + 4\epsilon^2$. H is diagonalized by a rotation through an angle θ where $\tan 2\theta = 2\epsilon$. Then the eigenvectors are columns of

$$U(\epsilon) = \frac{1}{\sqrt{D}} \begin{pmatrix} 1 & 2\epsilon \\ -2\epsilon & 1 \end{pmatrix}.$$

Clearly λ_{\pm} as well as the components of U have nice Taylor series expansions around $\epsilon = 0$.

Intuition: why does it work?

- Consider the $N \times N$ matrix $H(\epsilon) = H_0 + \epsilon H_1$. This is Hermitean, it is diagonalized by some unitary transformation $U(\epsilon)$ which lies in $SU(N)$.
- Every element of $SU(N)$ can be written as $\exp(\sum r_i \sigma_i)$, where r_i are real numbers and σ_i are Hermitean traceless matrices (there are $N(N-1)$ of these).
- As a result, the desired $U(\epsilon)$ can be reached by some continuous change of the r_i 's. This means that a series expansion of U in ϵ is always possible. So a series expansion of the eigenvectors in ϵ is always possible.
- The eigenvalues of $H(\epsilon)$ are obtained by the multiplication of three matrices, each of which admits a convergent series expansion in ϵ . So a series expansion of the eigenvalues should be possible.

Intuition: when does it not work?

It should be impossible to get bound states in a very weak potential by perturbation. In other words, if we take $H_0 = p^2/2m$ and $H_1 = V(r)$, bound states of $H = H_0 + \epsilon H_1$ cannot be expanded in a series in ϵ .

For example, take a quantum particle in one dimension. Let $V(r)$ be a square well with width a and depth ϵ . The bound state energy in such a well is

$$E \propto \epsilon^2.$$

However, this works only for $\epsilon < 0$. There are no bound states for $\epsilon > 0$. So the energy is not analytic in ϵ .

We will try to develop more intuition about when the perturbation series works and when it does not afterwards.

Outline

- 1 Outline
- 2 The set up
- 3 First order perturbation theory**
- 4 Second order perturbation theory
- 5 Keywords and References

First order perturbation theory

Equating the terms of the master equation linear in ϵ gives

$$(H_0 - E_i^0) |E_i^1\rangle = (E_i^1 - H^1) |E_i^0\rangle.$$

The operator on the left has one eigenvalue which vanishes. So the inverse does not exist! However, contraction with $\langle E_i^0 |$ immediately results in

$$E_i^1 = \langle E_i^0 | H_1 | E_i^0 \rangle + \langle E_i^0 | (H_0 - E_i^0) | E_i^1 \rangle = \langle E_i^0 | H_1 | E_i^0 \rangle.$$

To find the perturbed state, contract with $\langle E_j^0 |$, to obtain

$$\langle E_j^0 | E_i^1 \rangle = \frac{\langle E_j^0 | (E_i^1 - H_1) | E_i^0 \rangle}{E_j^0 - E_i^0}.$$

We have found the perturbed eigenstate when there are no degeneracies in the spectrum of H_0 . We will investigate the case with degeneracies later.

The same concrete example

Take, as before,

$$H_0 = \begin{pmatrix} 1 & 0 \\ 0 & 2 \end{pmatrix}, \quad H_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \text{so} \quad H(\epsilon) = \begin{pmatrix} 1 & \epsilon \\ \epsilon & 2 \end{pmatrix}.$$

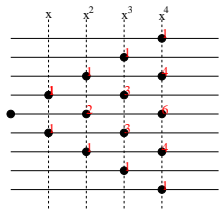
The eigenvectors of H_0 are $|1\rangle = (1, 0)^T$ and $|2\rangle = (0, 1)^T$. Since H_1 is off-diagonal in this basis, the perturbations to the eigenvalues are 0 to leading order. This agrees to leading order with the exact solution.

The perturbations to the eigenvectors are $\langle E_2^0 | E_1^1 \rangle = 1$ and $\langle E_1^0 | E_2^1 \rangle = -1$. This agrees with the series solution demonstrated earlier: $U_{11} = 1 + \mathcal{O}(\epsilon^2)$ and $U_{12} = \epsilon + \mathcal{O}(\epsilon^3)$. So the formulæ work as advertised.

Note the interesting fact that the perturbation does not change the energies but mixes the two original eigenstates.

Anharmonic potential

Perturb the harmonic oscillator potential by the anharmonic term $V(x) = \lambda x^4/4!$. Since $x = (a + a^\dagger)/\sqrt{2}$, the perturbation can also be written as $V = \lambda(a + a^\dagger)^4/96$. To find the first order shift in energy and wavefunction, we need to evaluate matrix elements such as $\langle m | V | n \rangle$. There is a nice diagrammatic method for this, which adapts the construction of **Pascal's triangle** to a harmonic oscillator. The horizontal lines are energy levels. As we apply more powers of $a + a^\dagger$, we move to the right, but also one step up or down.

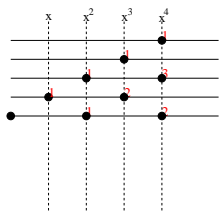


The number of ways of reaching a certain level after some number of steps is marked in red. So

$$\langle 5 | V | 5 \rangle = \frac{\lambda}{16}, \quad \text{but} \quad \langle 0 | V | 0 \rangle = \frac{\lambda}{48}.$$

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The perturbed wavefunction and renormalization

The perturbed ground state is

$$|0'\rangle = |0\rangle + \frac{\lambda}{32} |2\rangle + \frac{\lambda}{96} |4\rangle.$$

This state is not normalized, although the original states were. We need to perform the normalization again. The **renormalization constant** is

$$Z = \langle 0'|0'\rangle = 1 + \frac{5\lambda^2}{2.48^2}.$$

Application of perturbation theory always leads to a need to renormalize the wavefunction.

Generic states

Starting from the harmonic oscillator states $|1\rangle$, $|2\rangle$, $|3\rangle$, $|4\rangle$ and $|5\rangle$, find the perturbed energies, states and the wavefunction renormalization in first order due to a perturbation $\lambda x^4/4!$.

Non-invertible matrices

If a matrix A has a zero eigenvalue, then it has no inverse. This means that the equation $A|x\rangle = |y\rangle$ does not have a unique solution. If $A|v\rangle = 0$, i.e., $|v\rangle$ is a **null vector** of A , then from any solution $|X\rangle$ of the equation, we can generate an infinity of solutions $|X\rangle + \lambda|v\rangle$. We have a unique solution only if we insist that solutions have no component in the direction of $|v\rangle$. This is called **deflation**.

We form the **projection operator** $\Pi = |v\rangle\langle v|$. Now $\Pi|x\rangle$ is the projection of any vector $|x\rangle$ in the direction of $|v\rangle$. The projection orthogonal to this direction is $(1 - \Pi)|x\rangle$. So,

$$\text{if } A|x\rangle = |y\rangle \quad \text{then} \quad |x\rangle = (1 - \Pi)A^{-1}(1 - \Pi)|y\rangle,$$

where Π is the projection operator on the **null space** of A . This means that the deflated A gives a well-defined **pseudo-inverse** $(1 - \Pi)A^{-1}(1 - \Pi)$.

First order perturbation theory with degeneracy

In the equation

$$(H_0 - E_i^0) |E_i^1\rangle = (E_i^1 - H_1) |E_i^0\rangle,$$

the operator $H_0 - E_i^0$ has null-space $|E_i^0\rangle$. Denote the projector to the null-space to be Π_i . In this space, the equation becomes an eigenvalue equation for a 1×1 matrix, with solution

$E_i^1 = \text{Tr} \Pi_i H_1$. The vectors $|E_i^1\rangle$ are given by

$$|E_i^1\rangle = (1 - \Pi_i)(H_0 - E_i^0)^{-1}(1 - \Pi_i)(E_i^1 - H_1) |E_i^0\rangle.$$

Now suppose that the subspace of H_0 with eigenvalue H_0 is degenerate, spanned by (normalized) eigenvectors $|i\rangle$ (where $1 \leq i \leq n$). Then the projection operator on this subspace is $\Pi = \sum_i |i\rangle \langle i|$. The perturbed energies are then eigenvalues of the matrix $\Pi H_1 \Pi$. In this subspace we can find the solutions for the vectors.

An example

Choose

$$H_0 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \quad H_1 = \begin{pmatrix} 0 & 1 & 2 \\ 1 & 0 & 0 \\ 2 & 0 & 0 \end{pmatrix}.$$

Now $H_0 - 1$ has a null 2×2 block, so non-degenerate first order perturbation gives the equation $E^1 = \langle \lambda | H_1 | \lambda \rangle$, for any eigenstate H_0 in this space. This is incorrect. Also, there seems to be a vanishing energy denominator, giving infinite shifts in the perturbed state.

Instead, since H_0 has degenerate eigenvectors, one should use degenerate perturbation theory with

$$\Pi = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \Pi H_1 \Pi = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

The degenerate 2×2 block can be easily diagonalized.

Spin-orbit coupling

The **spin** \mathbf{S} of an electron gives rise to a magnetic moment $\vec{\mu} = -\mu_B g \mathbf{S}$ where the **Lande factor** $g \simeq 2$. If the electron belongs to the Hydrogen atom, then it experiences a magnetic field $\mathbf{B} = -\mathbf{v} \times \mathbf{E}$ due to the relative motion of the proton. As a result, there is a term

$$H' = -\boldsymbol{\mu} \cdot \mathbf{B} = \left(\frac{eg}{2m} \mathbf{S} \right) \cdot \left(\frac{Ze}{r^3} \mathbf{v} \times \mathbf{r} \right) = \left(\frac{Ze^2 g}{2m^2 r^3} \right) \mathbf{L} \cdot \mathbf{S}.$$

This is the **spin-orbit coupling** term.

An electron in the hydrogen atom has a state in the Hilbert space spanned by $|nlm\rangle \otimes |s\rangle = |nlms\rangle$. \mathbf{L} and \mathbf{S} commute since they act on different Hilbert spaces. As a result, H' does not spoil the rotational symmetry of the Coulomb Hamiltonian. Spin-orbit coupling splits the $n > 1$ states. Since $r \simeq a_0$, the magnitude of this splitting is of order $me^8 \simeq e^4 R$.

Problem 14.2: Fine structure of spectra

Examine the change in energies and states using degenerate first order perturbation theory. Define $\mathbf{J} = \mathbf{L} + \mathbf{S}$, and combine the states $|nlms\rangle$ via Clebsch-Gordan coefficients into states $|nljj_z\rangle$ where $\mathbf{J}^2 |nljj_z\rangle = j(j+1) |nljj_z\rangle$ and $J_z |nljj_z\rangle = j_z |nljj_z\rangle$. Carry out the computation within the degenerate subspace of a fixed n .

Perform the computation for $n = 1$ and 2 . Find how much of the degeneracy is lifted. Consult references to check whether your answers are quantitatively correct, or whether there are further effects left to be explained. Extend the computation, notionally, to all n and report the pattern of lifting of degeneracies.

What is the fine structure of spectra which is explained by such a perturbation theory?

Examples of spin-orbit coupling

Spin-orbit coupling of unpaired valence electrons in H or an alkali atom gives rise to visible splitting of spectral lines called the **fine structure of spectra**. For example the 10.2 eV transition from $|21m\rangle$ to the ground state $|100\rangle$ of H is split by $45 \mu\text{eV}$. Similarly the yellow light from the 2.1 eV transition of Na from $|31m\rangle$ states to the ground state $|200\rangle$ is split by 2.1 meV.

Atomic shells are filled when $Z = 2, 10, 28, \text{etc.}$. These are called **magic numbers**. In nuclei the magic numbers turn out to be 2, 8, 20, 28, 40 *etc.*. Maria Goppert-Meyer realized that these imply that the spin-orbit coupling term is negative; this led to the **nuclear shell model**.

In solids a local electric field can be induced by crystal symmetries or by creating artificial **heterostructures**. This is called the **Rashba effect**. This spin-orbit coupling strength can be manipulated.

Electron-nucleus interaction

Atomic states are specified by $|Elms\rangle \otimes |s'\rangle$ or $|nljj_z\rangle \otimes |s'\rangle$, where s' specifies the eigenvalues of \mathbf{I} , the spin of the nucleus. \mathbf{I} gives the nucleus a magnetic moment $\vec{\mu}_I = \gamma\mathbf{I}$, and γ is smaller than μ_B by the order of 1000. Nevertheless, the coupling of \mathbf{I} and \mathbf{J} degeneracy of the above atomic states to give coupled states $|nljff_z\rangle$ where f specifies the eigenvalues of \mathbf{F}^2 with $\mathbf{F} = \mathbf{J} + \mathbf{I}$. Note that \mathbf{L} , \mathbf{S} and \mathbf{I} operate on different Hilbert spaces and therefore commute.

The spin of the nucleus gives rise to a vector potential

$$\mathbf{A}_I = \frac{1}{r^3} \vec{\mu}_I \times \mathbf{r}, \quad \text{in the gauge } \nabla \cdot \mathbf{A}_I = 0.$$

The full Hamiltonian can then we separated into Coulomb and perturbation

$$H = \frac{1}{2m} (\mathbf{p} + e\mathbf{A}_I)^2 + V(\mathbf{r}) - \vec{\mu}_e \cdot (\nabla \times \mathbf{A}_I) = H_{\text{Coulomb}} + H'.$$

The perturbation term

To leading order in \mathbf{A}_I , we obtain

$$H' = \mu_B(\mathbf{p} \cdot \mathbf{A}_I + \mathbf{A}_I \cdot \mathbf{p}) - \vec{\mu}_e \cdot \nabla \times \mathbf{A}_I.$$

In the chosen gauge, we find

$$\mathbf{A}_I \cdot \mathbf{p} = \vec{\mu}_I \cdot \mathbf{r} \times \mathbf{p} = \frac{1}{r^3} \vec{\mu}_I \cdot \mathbf{L} = \frac{\gamma}{r^3} \mathbf{I} \cdot \mathbf{L}.$$

The second term can be rewritten using

$$\nabla \times \vec{\mu}_I \times \left(\frac{\mathbf{r}}{r^3} \right) = -\nabla \times \vec{\mu}_I \times \left(\nabla \frac{1}{r} \right).$$

The resultant term is

$$H'_2 = g\gamma\mu_B^2 \left[\left\{ (\mathbf{S} \cdot \nabla) \left(\mathbf{I} \cdot \nabla \frac{1}{r} \right) - \frac{1}{3} (\mathbf{S} \cdot \mathbf{I}) \nabla^2 \frac{1}{r} \right\} - \frac{2}{3} \mathbf{S} \cdot \mathbf{I} \nabla^2 \frac{1}{r} \right].$$

Problem 14.3: hyperfine structure

Show that the hyperfine interaction Hamiltonian becomes

$$H'_2 = -g\gamma\mu_B^2 \left[\left\{ -\frac{3\mathbf{S} \cdot \hat{\mathbf{r}} \mathbf{I} \cdot \hat{\mathbf{r}}}{r^3} + \frac{\mathbf{S} \cdot \mathbf{I}}{r^3} \right\} + \frac{8\pi}{3} \mathbf{S} \cdot \mathbf{I} \delta(\mathbf{r}) \right],$$

where the term in curly brackets vanishes in states with $l = 0$.

Estimate the order of magnitude by which the degeneracies of the states $|nljff_z\rangle$ is lifted for H by the above term, in terms of the powers of m , e , and the dimensionless constant $\lambda = m/M$ where m is the mass of the electron, e its charge, and M the mass of the proton.

Carry out the computation in first order perturbation theory and show the perturbed energies and the pattern of lifting of degeneracies.

Tensor terms

A term in the potential which contains the structure $(\mathbf{A} \cdot \hat{\mathbf{r}})(\mathbf{B} \cdot \hat{\mathbf{r}})$ is called a **tensor potential**. The nomenclature comes from the fact that $\hat{\mathbf{r}}\hat{\mathbf{r}}$ is a rotational tensor, as can be seen by examining its commutator with \mathbf{L} . As a result, it ladders between states of j , $j + 1$ and $j + 2$.

A tensor term in the potential typically arises from the interaction of two particles each of which can be characterized by a vector, such as the spin. In electromagnetic interactions they arise from the interactions of two dipoles.

Such a term arises in the study of the **hyperfine structure** of atomic spectra, as we have just examined. It also arises in the study of **nucleon-nucleon potentials**. There it is responsible for the admixture of a $l = 2$ state into the ground state of the Deuterium nucleus (^2H). Check whether this can also happen for the H atom.

Outline

- 1 Outline
- 2 The set up
- 3 First order perturbation theory
- 4 Second order perturbation theory**
- 5 Keywords and References

Second order perturbation theory

From the master equation for the perturbations, extract the quadratic terms in ϵ . These give

$$(H_0 - E_i^0) |E_i^2\rangle = E_i^2 |E_i^0\rangle - (H_1 - E_i^1) |E_i^1\rangle.$$

Assuming that H_0 has no degeneracies, we can project on to the state $|E_i^0\rangle$ to obtain

$$\begin{aligned} E_i^2 &= \langle E_i^0 | H_1 - E_i^1 | E_i^1 \rangle = \langle E_i^0 | (H_1 - E_i^1) \tilde{\Delta}_i (H_1 - E_i^1) | E_i^0 \rangle \\ &= \langle E_i^0 | H_1 | E_i^0 \rangle + \sum_{j \neq i} \frac{|\langle E_i^0 | H_1 | E_j^0 \rangle|^2}{E_i^0 - E_j^0} \end{aligned}$$

where $\tilde{\Delta}_i = (1 - \Pi_i)(H_0 - E_i^0)^{-1}(1 - \Pi_i)$. The orthogonal projection gives

$$|E_i^2\rangle = \tilde{\Delta}_i (E_i^1 - H_1) \tilde{\Delta}_i (E_i^1 - H_1) |E_i^0\rangle.$$

Higher orders in perturbation theory

From the ϵ^n terms in the master equation we obtain

$$(H_0 - E_0) |E_i^n\rangle + (H_1 - E_i^1) |E_i^{n-1}\rangle = \sum_{\ell=2}^n E_i^\ell |E_i^{n-\ell}\rangle.$$

Using the projector Π_i , we have

$$E_i^n = \langle E_i^0 | H_1 - E_i^1 | E_i^{n-1} \rangle - \sum_{\ell=2}^{n-1} E_i^\ell \langle E_i^0 | E_i^{n-\ell} \rangle.$$

The orthogonal projection gives the eigenvector

$$|E_i^n\rangle = \tilde{\Delta}_i (E_i^1 - H_1) |E_i^{n-1}\rangle - \sum_{\ell=2}^{n-1} \tilde{\Delta}_i E_i^\ell |E_i^{n-\ell}\rangle.$$

Stark effect

The **Stark effect** is the shift of energy levels in an atom placed in an external electric field, \mathbf{E} . The perturbation Hamiltonian is

$$H_1 = -e\mathbf{r} \cdot \mathbf{E}, \quad \text{where} \quad H_0 = \frac{p^2}{2m} - \frac{e^2}{r}.$$

Consider the parity operation, P , which has the effect $P\mathbf{r} = -\mathbf{r}$ and $P\mathbf{p} = -\mathbf{p}$. Note that $P^2 = 1$, so that P has eigenvalues ± 1 . As a result, P is both Hermitean and unitary. Now, $[P, H_0] = 0$, and $P|nlm\rangle = (-1)^l|nlm\rangle$. However, $PH_1P = -H_1$. As a result, $\langle nlm|H_1|nlm\rangle = 0$. So $E_{nlm}^1 = 0$.

Problem 14.4

Set up degenerate 2nd order perturbation theory using the notation of these lectures. Apply it to find the lifting of degeneracies due to the Stark effect.

Outline

- 1 Outline
- 2 The set up
- 3 First order perturbation theory
- 4 Second order perturbation theory
- 5 Keywords and References**

Keywords and References

Keywords

Lorentz force, cyclotron frequency, magnetic moment, Bohr magneton, gyromagnetic ratio, hydrogenic atom, Magnetars, Pascal's triangle, renormalization constant, null vector, matrix deflation, projection operator, null space, pseudo-inverse, spin, Lande factor, spin-orbit coupling, fine structure of spectra, magic numbers, nuclear shell model, semiconductor heterostructures, Rashba effect, tensor potential, hyperfine structure, nucleon-nucleon potentials.

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