Atomic Physics Notes

Shaojun Zan

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Contents

Part I

Atomic Structure

1 Introduction

1.1 Overview

Atomic physics is disgusting, but in a different way from EM part 2. More specifically, EM part 2 is the second year of atrocity of oscillations and waves, especially optics; on the other hand, atomic physics gets notorious by its hydrodynamics-ish formulas and expressions.

In this part of notes we will mainly investigate the hydrogen atom. The multiple structures of hydrogen atom consider the terms influencing the energy in the following cladogram:
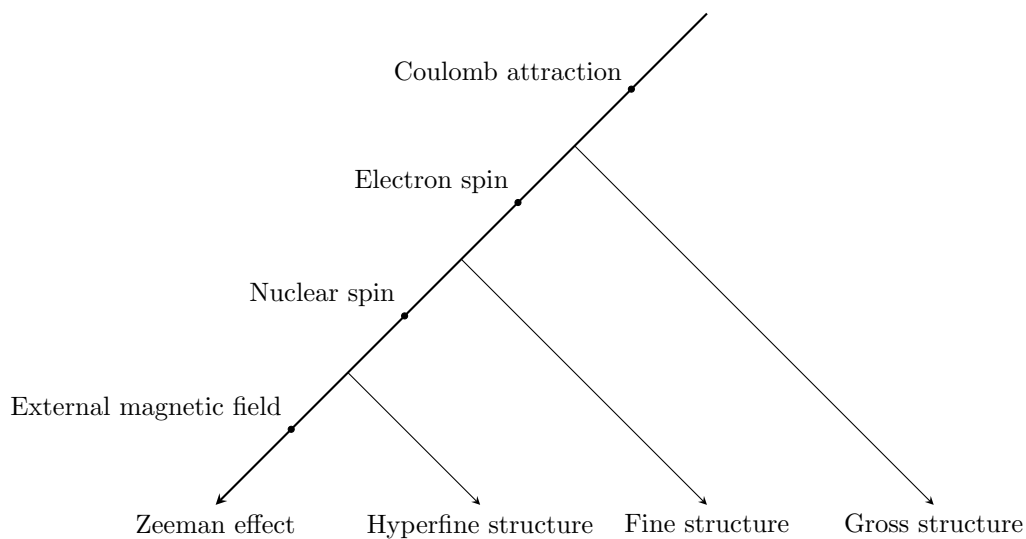
1.2 Addition of Angular Momenta

If two distinct physical systems or two distinct sets of dynamical variables of one system, which are described in two different vector spaces, are merged, the states of the composite system are vectors in the direct product space of the two previously separate vector spaces. The operator,

$$\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 \otimes \mathbb{1}_2 + \mathbb{1}_1 \otimes \hat{\mathbf{J}}_2, \tag{1}$$

or more simply (less accurately),

$$\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2, \tag{2}$$

is called the total angular momentum of the composite system. Note that the angular momentum here refers to any abstract operators that satisfy commutation relations, i.e. angular momentum and spin. We can check the commutation relations:

$$\left[\hat{J}_i, \hat{J}_j\right] = i\hbar\epsilon_{ijk}\hat{J}_k$$
$$\left[\hat{J}_z, \hat{J}_1^2\right] = \left[\hat{J}_z, \hat{J}_2^2\right] = \left[\hat{J}^2, \hat{J}_1^2\right] = \left[\hat{J}^2, \hat{J}_1^2\right] = 0. \tag{3}$$

The problem of the addition of two angular momenta consists of obtaining the eigenvalues of $\hat{J}_z$ and $\hat{J}^2$ and their eigenvectors in terms of the direct product of the eigenvectors of $\hat{J}_{1z}$, $\hat{J}_1^2$ and $\hat{J}_{2z}$, $\hat{J}_2^2$. Firstly, the simultaneous eigenkets:

$$|j_1 j_2 m_1 m_2\rangle = |j_1 m_1\rangle \otimes |j_2 m_2\rangle = |j_1 m_1\rangle |j_2 m_2\rangle. \tag{4}$$

These normalized eigenkets form a basis in the product space. From this basis, we aim to find the eigenvectors of $\hat{J}_z$, $\hat{J}^2$, which form a new basis: $|j_1 j_2 jm\rangle$. By the completeness relation, we see

$$|j_1 j_2 jm\rangle = \sum_{m_1, m_2} |j_1 j_2 m_1 m_2\rangle \langle j_1 j_2 m_1 m_2 | j_1 j_2 jm\rangle. \tag{5}$$

Accordingly, the problem reduces to finding the transformation coefficients (Clebsch-Gordan):

$$\langle j_1 j_2 m_1 m_2 | j_1 j_2 jm\rangle \equiv \langle m_1 m_2 | jm\rangle, \tag{6}$$

for the sake of simplifying notations.

Now, we investigate the action of $\hat{J}_z = \hat{J}_{1z} + \hat{J}_{2z}$ on the new basis. The LHS and RHS of (5) gives:

$$\hat{J}_z |j_1 j_2 jm\rangle = m\hbar |j_1 j_2 jm\rangle$$
$$\left(\hat{J}_{1z} + \hat{J}_{2z}\right) |j_1 j_2 m_1 m_2\rangle = (m_1 + m_2)\hbar |j_1 j_2 m_1 m_2\rangle.$$

Immediately follows is the **selection rule**:

$$\langle j_1 j_2 m_1 m_2 | j_1 j_2 jm\rangle = 0 \quad \text{if} \quad m \neq m_1 + m_2. \tag{7}$$

If we apply the ladder operators on the new basis, we get

$$\sqrt{(j \pm m)(j \mp m + 1)}\,\langle m_1 m_2 | j, m \mp 1\rangle = \sqrt{(j_1 \mp m_1)(j_1 \pm m_1 + 1)}\,\langle m_1 \pm 1, m_2 | jm\rangle$$
$$+ \sqrt{(j_2 \mp m_2)(j_2 \pm m_2 + 1)}\,\langle m_1, m_2 \pm 1 | jm\rangle. \tag{8}$$

More specifically, if we take $m = j$ and $m_1 = j_1$, then

$$\sqrt{2j} \, \langle j_1, j - j_1 - 1 | j, j - 1 \rangle = \sqrt{(j_2 - j + j_1 + 1)(j_2 + j - j_1)} \, \langle j_1, j - j_1 | jj \rangle. \tag{9}$$

This means if we know $\langle j_1, j - j_1 | jj \rangle$, then we know $\langle j_1, j - j_1 - 1 | j, j - 1 \rangle$ and $\langle j_1 - 1, j - j_1 | j, j - 1 \rangle$. Continuing in this manner, we can generate a tower of values from the term

$$\langle j_1 j_2 j_1, j - j_1 | j_1 j_2 jj \rangle. \tag{10}$$

Clearly, the fourth entry of the bra takes values in the range

$$-j_2 \leq j - j_1 \leq j_2 \quad \Rightarrow \quad j_1 - j_2 \leq j \leq j_1 + j_2.$$

Since j_1 and j_2 are on a symmetric footing, we could equally well have expressed all the C-G coefficients in terms of $\langle j_1 j_2, j - j_2, j_2 | j_1 j_2 jj \rangle$. This leads to

$$j_2 - j_1 \leq j \leq j_1 + j_2.$$

Therefore, we get the **triangular condition**:

$$|j_1 - j_2| \leq j \leq j_1 + j_2. \tag{11}$$

Since $m = m_1 + m_2$ ranges between $-j$ and j, it follows that j takes values from $|j_1 - j_2|$ to $j_1 + j_2$ in integer steps. Hence, either all three quantum numbers j_1, j_2, and j are integers, or two of them are half-integral and one is an integer.

2 Hydrogen Gross Structure

2.1 Hamiltonian in Center-of-mass Frame

Considering only Coulombic attraction, the Hamiltonian is

$$\hat{\mathcal{H}} = \left(\frac{-\hbar^2}{2m_p}\nabla_p^2\right) + \left(\frac{-\hbar^2}{2m_e}\nabla_e^2\right) + \left(\frac{-e^2}{4\pi\epsilon_0}\frac{1}{\|\mathbf{r}_e - \mathbf{r}_p\|}\right). \tag{12}$$

The problem is better solved with the center-of-mass frame. By defining

$$M = m_e + m_p \qquad\qquad \text{total mass}$$
$$\mathbf{R} = \frac{m_e\mathbf{r}_e + m_p\mathbf{r}_p}{M} \qquad\qquad \text{center-of-mass position}$$
$$m = \frac{m_e m_p}{m_e + m_p} \qquad\qquad \text{reduced mass}$$
$$\mathbf{r} = \mathbf{r}_e - \mathbf{r}_p \qquad\qquad \text{relative electron position,}$$

we find the Hamiltonian in the center-of-mass frame:

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_c + \hat{\mathcal{H}}$$
$$= \frac{-\hbar^2}{2M}\nabla_R^2 + \frac{-\hbar^2}{2m}\nabla_r^2 + \frac{-e^2}{4\pi\epsilon_0}\frac{1}{\|\mathbf{r}\|}. \tag{13}$$

The problem nicely separates: the first term concerns how the atom moves as a whole, so we will only focus on the second part, which describes the internal interaction. The total solution is simply the product of internal and center-of-mass solutions.

2.2 A Natural Scale for Distance

Clearly, this is a problem in the central potential, and the solution is

$$u(r,\theta,\phi) = R(r)Y_{lm}(\theta,\phi) = \frac{1}{r}\chi(r)Y_{lm}(\theta,\phi). \tag{14}$$

Through the variable substitution $R(r) = \chi(r)/r$, one reduce the radial part of laplacian in spherical coordinates into a simple second derivative:

$$\left[\frac{-\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{l(l+1)\hbar^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\right]\chi(r) = E\chi(r). \tag{15}$$

This suggests that the quantities $\left(\frac{e^2}{4\pi\epsilon_0}\frac{1}{a_0}\right)$ and $\left(\frac{\hbar^2}{ma_0^2}\right)$ both have the dimension of energy. Therefore,

we may equate these two and solve for a_0:

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Bohr Radius

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{e^2 m} \approx 5.3 \times 10^{-11}\,\text{m} \tag{16}$$

is called the **effective Bohr radius** (m here is the reduced mass). If m is the electron mass, then a_0 is the Bohr radius in Bohr's atomic model.

By considering the masses of electron and proton,

$$
\begin{aligned}
m_e &= 9.1 \times 10^{-31}\,\text{kg} = 0.51\,\text{MeV/c}^2 \\
m_p &= 1.7 \times 10^{-27}\,\text{kg} = 940\,\text{MeV/c}^2,
\end{aligned}
\tag{17}
$$

the approximation of $m \approx m_e$ is accurate to better than 0.1%.

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2.3 A Natural Scale for Energy

With the scaled distance $r_0 = r/a_0$ owing to the effective Bohr radius, we have

$$\frac{1}{2}\alpha^2 mc^2\left[-\frac{\mathrm{d}^2}{\mathrm{d}r_0^2} + l(l+1)\frac{1}{r_0^2} - \frac{2}{r_0}\right]\chi(r) = E\chi(r). \tag{18}$$

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The dimensionless quantity

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} = 0.007297\ldots \approx \frac{1}{137} \tag{19}$$

is called the **fine structure constant**. The prefactor in (18) sets the energy scale of the gross structure (and thus the atom as a whole):

$$\frac{1}{2}\alpha^2 mc^2 \approx 13.6\,\text{eV}. \tag{20}$$
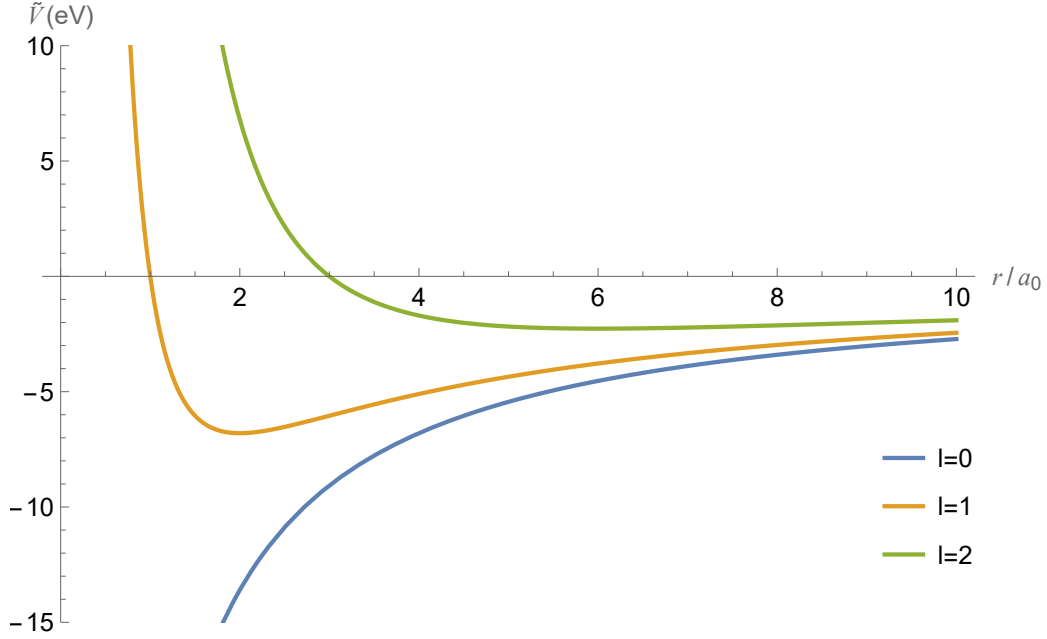
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2.4 Effective Potential

By including the rotational kinetic energy, we find the **effective potential**:

$$\tilde{V}(r) = \frac{1}{2}\alpha^2 mc^2\left[l(l+1)\frac{1}{r_0^2} - \frac{2}{r_0}\right], \tag{21}$$

and therefore,

$$\left[\frac{-\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \tilde{V}(r)\right]\chi(r) = E\chi(r). \tag{22}$$

The following plot shows the effective potentials. The $l = 1$ curve has its minimum at $r = 2a_0$, and $l = 2$, $r = 6a_0$.

2.5 Radial Eigenfunctions & Eigenvalues

Before we actually solve the Schrödinger equation (18), which we won't, we may compare this situation to a 1D infinite square well: $\chi(0) = 0$ for the energy to be finite, and $\chi(\infty) \to 0$ for the function to be normalizable. It's like the infinite square well problem with boundaries set near $r \to 0$ and $r \to \infty$.

Hence, the solutions should resemble those in infinite square well: the ground state eigenfunction will not cross the real axis, while the first excited state crosses once, and so on.

The solutions are labeled by χ_{kl}, where k is the number of nodes, $k \geq 1$ for $\chi(0) = 0$.

There is no obvious relationship between k and l. Different l suggests different effective potentials, while k labels the corresponding solutions with different energies.

The energy eigenvalues are

$$E = -\frac{1}{2}\alpha^2 mc^2 \frac{1}{(k+l)^2},\tag{23}$$

and this accidental degeneracy of k and l leads to the definition of principal quantum number n:

$$n = k + l.\tag{24}$$

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Therefore, in a hydrogen atom, the energy eigenvalue is solely determined by its principal quantum number:

$$E_n = -\frac{1}{2}\alpha^2 mc^2 \frac{1}{n^2} \approx -13.6\,\text{eV}\,\frac{1}{n^2}. \tag{25}$$

From the above discussions, we know that $n = k + l > 0$, and $l < n$ for $k > 0$.

Remember the variable substitution at the beginning? Now we're going to substitute it back:

$$R_{nl} = \frac{1}{r}\chi_{n-l,l} = N_{nl}\left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}\left[\frac{2r}{na_0}\right]\exp\left(-\frac{r}{na_0}\right), \tag{26}$$

where L_i^m is the associated Laguerre polynomial.

- All R_{nl} have the form of a polynomial in r, of order $n - 1$, multiplied by an exponential with decay length na_0.

- If $l = 0$, then the Laguerre polynomials carry a constant term, which implies $R_{n0} > 0$ for all n values. This also means $R_{nl} = 0$ for any $l > 0$. This is different from $\chi(r)$, all of which have a node at $r = 0$.

2.6 The Total Eigenfunction

The total eigenfunctions are given by

$$u_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi), \tag{27}$$

where Y_{lm} is the spherical harmonics, with the associated Legendre polynomials of $\cos\theta$ in θ direction.

We can also work out the size of the ground state:

$$\langle r \rangle = \int dV\, r|u_{100}|^2 = \int_0^\infty dr\, r^3 |R_{10}(r)|^2 = \frac{3}{2}a_0.$$

3 Helium Gross Structure

3.1 Two-electron States

Due to the fundamental indistinguishability of quantum particles, it is impossible for us to keep track of the electrons. Therefore, states like $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$ are meaningless.

To study this issue more carefully, consider the exchange operator $\hat{P}$:

$$\hat{P}\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_2, \mathbf{r}_1). \tag{28}$$

If the particles are identical, then this operator should not change the state in a meaningful way. Hence, a valid two-electron state must satisfy

$$\psi(\mathbf{r}_2, \mathbf{r}_1) = \lambda\psi(\mathbf{r}_1, \mathbf{r}_2) \quad \text{with} \quad |\lambda| = 1. \tag{29}$$

The above two equations together imply that ψ is an eigenstate of $\hat{P}$. If we apply $\hat{P}$ on ψ twice, then we see $\lambda = \pm 1$.

> If $\lambda = 1$, then we say the wavefunction is **symmetric**, and if $\lambda = -1$ means an **antisymmetric** wavefunction.
>
> If the particles are indistinguishable, then the Hamiltonian must treat them in the same way. This suggests $\left[\hat{\mathcal{H}}, \hat{P}\right] = 0$: if a two-particle wavefunction is symmetric, it remains symmetric for all time. Bosons are symmetric with respect to exchange, while fermions are antisymmetric.

With the above discussions, we know we cannot stick to the original set of compatible observables $\left\{s_1^2, s_{1z}, s_2^2, s_{2z}\right\}$ in two-electron states, as it is impossible to tell which electron is which. Instead, we define the total spin

$$\hat{\mathbf{S}} = \hat{\mathbf{s}}_1 + \hat{\mathbf{s}}_2, \tag{30}$$

which leads us to the new basis of compatible observables

$$\left\{\hat{S}^2, \hat{S}_z, \hat{s}_1^2, \hat{s}_2^2\right\}. \tag{31}$$

As $\hat{s}_1^2$ and $\hat{s}_2^2$ have unchanging definite values for electrons, we shall always denote our states with $|S, M_S\rangle$:

$$\hat{S}^2 |S, M_S\rangle = \hbar^2 S(S+1) |S, M_S\rangle$$
$$\hat{S}_z |S, M_S\rangle = \hbar M_S |S, M_S\rangle. \tag{32}$$

The above also implies commutations like $\left[\hat{S}^2, \hat{s}_{1z}\right] \neq 0$. For our base kets to be valid, we construct symmetric and antisymmetric states (in terms of exchange operator) to avoid the indistinguishability:

$$
\begin{cases} |\uparrow\downarrow\rangle \\ |\downarrow\uparrow\rangle \end{cases} \Rightarrow \begin{cases} \dfrac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right) & \text{Symmetric} \\[2ex] \dfrac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) & \text{Antisymmetric} \end{cases}
\tag{33}
$$

The following table summarizes the four states written in total spin basis:

Single-spin Kets	Total-spin Kets	Exchange Symmetry
$|\uparrow\uparrow\rangle$	$|1,1\rangle$	Symmetric
$\dfrac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)$	$|1,0\rangle$	Symmetric
$|\downarrow\downarrow\rangle$	$|1,-1\rangle$	Symmetric
$\dfrac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$	$|0,0\rangle$	Antisymmetric

3.2   Position & Spin

We know that electrons are antisymmetric with respect to exchange. Therefore, if we write the total wavefunction as

$$
\psi(\mathbf{r}_1, \mathbf{s}_1; \mathbf{r}_2, \mathbf{s}_2) = \phi(\mathbf{r}_1, \mathbf{r}_2)\chi(\mathbf{s}_1, \mathbf{s}_2),
\tag{34}
$$

then we must have

$$
\hat{P}\psi(\mathbf{r}_1, \mathbf{s}_1; \mathbf{r}_2, \mathbf{s}_2) = \psi(\mathbf{r}_2, \mathbf{s}_2; \mathbf{r}_1, \mathbf{s}_1)
$$

$$
-\phi(\mathbf{r}_1, \mathbf{r}_2)\chi(\mathbf{s}_1, \mathbf{s}_2) = \left[\hat{P}\phi(\mathbf{r}_1, \mathbf{r}_2)\right]\left[\hat{P}\chi(\mathbf{s}_1, \mathbf{s}_2)\right],
$$

and this means

$$
\lambda_\phi \lambda_\chi = -1.
\tag{35}
$$

In other words, if the spatial wavefunction is symmetric, then the spin state has to be antisymmetric, and vice versa. To construct wavefunctions with symmetry, we use

$$
\phi_S(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}\left[\alpha(\mathbf{r}_1)\beta(\mathbf{r}_2) + \alpha(\mathbf{r}_2)\beta(\mathbf{r}_1)\right]
$$

$$
\phi_A(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}\left[\alpha(\mathbf{r}_1)\beta(\mathbf{r}_2) - \alpha(\mathbf{r}_2)\beta(\mathbf{r}_1)\right],
\tag{36}
$$

if one electron is in state α, and the other in β.

The possible two-electron states are thus

$$\phi_S \chi_{0,0} \quad \text{and} \quad \phi_A \chi_{1,i}. \tag{37}$$

Therefore, in dirac notation, we choose the two wavefunctions and the total spin to specify a two-electron state:

$$|\alpha, \beta, S, M_S\rangle. \tag{38}$$

Particularly, if we have the two electrons in the same spatial state, then it is impossible to construct an antisymmetric wavefunction. Consequently, they must be in the $S = 0$ total spin state.

3.3   Helium Hamiltonian

We could treat the nucleus simply as a particle with a particular charge, mass, and spin. In the gross structure of Helium,

$$\hat{\mathcal{H}} = \left(\frac{-\hbar^2}{2m_n}\nabla_n^2\right) + \sum_{i=1}^{2}\left(-\frac{-\hbar^2}{2m_e}\nabla_i^2 + \frac{-Ze^2}{4\pi\epsilon_0}\frac{1}{\|\mathbf{r}_i - \mathbf{r}_n\|}\right) + \left(\frac{e^2}{4\pi\epsilon_0}\frac{1}{\|\mathbf{r}_1 - \mathbf{r}_2\|}\right), \tag{39}$$

where Z is the nuclear charge. By assuming the nucleus stationary at the origin, we treat the electron-electron repulsion as a perturbation:

$$\begin{aligned}
\hat{\mathcal{H}}' &= \sum_{i=1}^{2}\left(-\frac{-\hbar^2}{2m_e}\nabla_i^2 + \frac{-Ze^2}{4\pi\epsilon_0}\frac{1}{\|\mathbf{r}_i - \mathbf{r}_n\|}\right) + \left(\frac{e^2}{4\pi\epsilon_0}\frac{1}{\|\mathbf{r}_1 - \mathbf{r}_2\|}\right) \\
&= \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_1.
\end{aligned} \tag{40}$$

3.4   Ground State

$\hat{\mathcal{H}}_0$ is the sum of separate hydrogen-like Hamiltonians for each electron, so the zeroth-order perturbation theory gives

$$U_g(\mathbf{r}_1, \mathbf{r}_2) = u_{100}(\mathbf{r}_1)u_{100}(\mathbf{r}_2), \tag{41}$$

where u_{100} is a hydrogenic function. Looking back to our hydrogen solutions, we know the energy in ground state is given by

$$E_1 = -\frac{1}{2}\alpha^2 mc^2 = -\frac{1}{2}\left(\frac{e^2}{4\pi\epsilon_0 \hbar c}\right)^2 mc^2.$$

In this case where $Z = 2$, α is scaled by $Z^2 = 4$, and two electrons have an energy of

$$E = 2 \cdot Z^2 \left(-\frac{1}{2}\alpha^2 m_e c^2\right) \approx -108.8\,\text{eV}. \tag{42}$$

Therefore, the energy of perturbation is given by the first-order perturbation theory:

$$\delta E_g = \left\langle U_g \middle| \hat{\mathcal{H}}_1 U_g \right\rangle = \frac{e^2}{4\pi\epsilon_0} \iint \mathrm{d}\mathbf{r}_1 \, \mathrm{d}\mathbf{r}_2 \, \frac{1}{\|\mathbf{r}_1 - \mathbf{r}_2\|} |U_g|^2 = \frac{5}{16}|E_g|. \tag{43}$$

This first-order perturbation modifies the energy to be $-74.8\,\mathrm{eV}$, while the true value is $-79\,\mathrm{eV}$. We can also calculate the energy required to make the He^+:

$$E' = E_{n=1} - E'_g = 24.5\,\mathrm{eV}. \tag{44}$$

3.5 Excited State

We will consider the situation with one excited electron and one ground state electron. There cannot be two excited electrons, or the He atom will be unstable and decay into a free electron and a He^+.

In the case of only one excited electron, we make valid electron states $\phi_\pm$ with (36). Therefore,

$$\delta E_\pm = \left\langle \phi_\pm \middle| \hat{\mathcal{H}}_1 \phi_\pm \right\rangle = J \pm K, \tag{45}$$

where we define the direct integral J and exchange integral K:

$$\begin{aligned}
J &= \frac{1}{2}\left(\left\langle ge \middle| \hat{\mathcal{H}}_1 ge \right\rangle + \left\langle eg \middle| \hat{\mathcal{H}}_1 eg \right\rangle\right) = \left\langle ge \middle| \hat{\mathcal{H}}_1 ge \right\rangle \\
K &= \frac{1}{2}\left(\left\langle ge \middle| \hat{\mathcal{H}}_1 eg \right\rangle + \left\langle eg \middle| \hat{\mathcal{H}}_1 ge \right\rangle\right) = \mathrm{Re}\left(\left\langle eg \middle| \hat{\mathcal{H}}_1 ge \right\rangle\right),
\end{aligned} \tag{46}$$

where g and e respectively mean ground and excited states. J can interpreted as the mean electric potential energy of two charges with probability densities $|u_g|^2$ and $|u_e|^2$, while K has no obvious classical interpretations. Also, $J > K$.

To summarize, all of the four states share the same energy without first-order corrections. If the correction is considered, then the antisymmetric state has a lower energy.

In conventional nomenclature, quantum number n may refer to a shell of electrons, while the set (n, l) refers to a specific subshell. By denoting l by specific letters (s, p, d, f, g, and so on), we can write out the ground state electron configuration for a multiple-electron atom.

4 Hydrogen Molecular Ion

4.1 Hamiltonian

To begin with, we assume that the protons are essentially stationary. Let the origin be the midpoint connecting the protons and the distance between the protons be $\mathbf{R}$.
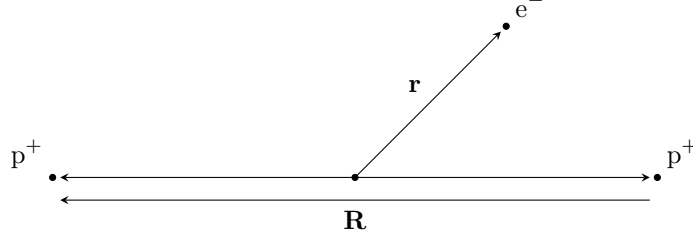
Therefore, the Hamiltonian should be written as

$$\hat{\mathcal{H}} = \left(\frac{-\hbar^2}{2m_e} \nabla_r^2 \right) + \frac{-e^2}{4\pi\epsilon_0} \left(\frac{1}{\|\mathbf{r} - \mathbf{R}/2\|} + \frac{1}{\|\mathbf{r} + \mathbf{R}/2\|} \right) + \left(\frac{e^2}{4\pi\epsilon_0} \frac{1}{\|\mathbf{R}\|} \right). \tag{47}$$

We also assume that the protons are far apart: $\|\mathbf{R}\| \gg a_0$. Therefore, the ground state is essentially a hydrogen atom with a proton far apart. Therefore, the hydrogen eigenstates can be the approximate solutions to the ground state.

Combining these ideas, we make the ground state and first excited state solution to be the even and odd combinations of hydrogen ground state solution:

$$\begin{aligned}
u_+(\mathbf{r}) &= N_+ \left[u_{100}(\mathbf{r} - \mathbf{R}/2) + u_{100}(\mathbf{r} + \mathbf{R}/2) \right] && \text{Ground state} \\
u_-(\mathbf{r}) &= N_- \left[u_{100}(\mathbf{r} - \mathbf{R}/2) - u_{100}(\mathbf{r} + \mathbf{R}/2) \right] && \text{First excited state.}
\end{aligned} \tag{48}$$

4.2 Molecular Bonding

The true ground state has a minimum at $R = 2a_0$, which corresponds to a molecular bond; while the first excited state has no minimum. Therefore, u_+ is called a bonding orbital, while u_-, an antibonding orbital.

The H_2^+ ion also has higher energy electronic states, which are similarly approximated to be a linear combination of two hydrogenic wavefunctions. Each (n, l, m) yields a bonding and antibonding orbital, each of which has a unique energy curve.

4.2.1 Molecular Hydrogen

There are two protons and two electrons. In the ground state, both electrons occupy the 1s-1s bonding orbital (u_+). Since the electrons have identical spatial wavefunction, the total spin must be $S = 0$. The

binding energy, with two electrons being shared, is $4.8\,\text{eV}$. We can understand this as twice the $\text{H}_2{}^+$ binding energy $(2.8\,\text{eV})$, reduced by electron-electron repulsion.

4.2.2 Helium

There are two nuclei and four electrons. If the atoms bind together, then two electrons are in 1s-1s bonding orbital, while the other two are in 1s-1s antibonding orbital. The total energy is comparable to that of two separate helium atoms, so no significant bond is formed.

4.2.3 Molecular Oxygen

The electron configuration of an oxygen atom is $1\text{s}^2 2\text{s}^2 2\text{p}^4$, which has 4 valence electrons. For two oxygen atoms, the three 2p orbitals from each atom combine to form 3 bonding orbitals and 3 antibonding orbitals. Therefore, of the 8 total valence electrons, 6 fill the bonding orbitals, and 2 occupy the antibonding orbitals. There is an overall decrease in energy: loosely speaking, there is a net of two bonds ("double bond").

4.3 Molecular Motion

Since nuclear motion is relatively slow, the electron remains in the ground state. Using our trick of center-of-mass frame, we focus on the internal motion of two protons. The electron now plays the role of providing the potential energy:

$$\hat{\mathcal{H}}_n = \frac{-\hbar^2}{2\mu}\nabla_{\mathbf{R}}^2 + E_+(R). \tag{49}$$

Clearly, this is again a central potential, and we have

$$\psi(R,\theta,\phi) = \frac{1}{R}\chi(R)Y_{lm}(\theta,\phi)$$

with

$$\left[\frac{-\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}R^2} + \frac{l(l+1)\hbar^2}{2\mu R^2} + E_+(R)\right]\chi(R) = E\chi(R). \tag{50}$$

Unless the molecule is in a highly excited state, $\psi(R,\theta,\phi)$ will be nonzero only for R close to the bond length R_0. This allows us to simplify with the approximations:

$$\frac{l(l+1)\hbar^2}{2\mu R^2} \approx \frac{l(l+1)\hbar^2}{2\mu R_0^2}, \qquad E_+(R) \approx E_+(R_0) + \frac{1}{2}\mu\omega_v^2(R-R_0)^2. \tag{51}$$

Hence, we find this problem similar to the harmonic oscillator:

$$E = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}} = E_+(R_0) + \frac{1}{2}\hbar\omega_v\left(n+\frac{1}{2}\right) + \frac{l(l+1)\hbar^2}{2\mu R_0^2}. \tag{52}$$

5 Hydrogen Fine Structure

5.1 Spin-orbit Interaction

The fine structure of hydrogen consider the electron spin:

$$\hat{\mu} = -\frac{g_e \mu_{\mathrm{B}} \hat{\mathbf{s}}}{\hbar} \approx -\frac{2\mu_{\mathrm{B}} \hat{\mathbf{s}}}{\hbar} \quad \text{with} \quad \mu_{\mathrm{B}} = \frac{e\hbar}{2m_e} \text{ (Bohr magneton)}. \tag{53}$$

There is an energy due to the interaction of an electron with a magnetic field, as described by

$$\hat{\mathcal{H}} = -\hat{\mu} \cdot \mathbf{B}. \tag{54}$$

In the frame of the electron, the proton is moving, and moving charges create magnetic fields. Actually, a particle moving at velocity $\mathbf{v}$ through an electric field $\mathbf{E}$ experiences a magnetic field

$$\mathbf{B} = -\frac{\mathbf{v} \times \mathbf{E}}{c^2}. \tag{55}$$

Therefore, we get the spin-orbit interaction Hamiltonian:

$$\hat{\mathcal{H}}_s = \alpha^2 \left(\frac{1}{2}\alpha^2 m_e c^2\right) \left(\frac{a_0^3}{r^3}\right) \frac{\hat{\mathbf{s}} \cdot \hat{\boldsymbol{\ell}}}{\hbar^2}. \tag{56}$$

We see from above that the natural energy scale for the spin-orbit interaction is a factor of α^2 smaller than the gross energy scale. This is why we call α the fine structure constant.

5.2 Degenerate Perturbation Theory

We know the energy scale of spin-orbit interaction, so we should treat this as a perturbation. However, the energies are degenerate, so we must use degenerate perturbation theory.

We need to use gross-structure eigenstates that are also eigenstates of $\hat{\mathcal{H}}_s$ within each degenerate eigenspace of the gross-structure Hamiltonian.

As the gross-structure energy only depends on n, the degenerate eigenspace is formed by the states of different possible values of (l, m_l, m_s).

Before moving on, we can still do some simplification. For the states with quantum numbers n and l,

$$\left\langle \frac{a_0^3}{r^3} \right\rangle_{nl} = \frac{1}{l(l+1/2)(l+1)n^3} \equiv \beta_{nl} \quad \Rightarrow \quad \hat{\mathcal{H}}_s = \alpha^2 \left(\frac{1}{2}\alpha^2 m_e c^2\right) \beta_{nl} \frac{\hat{\mathbf{s}} \cdot \hat{\boldsymbol{\ell}}}{\hbar^2}. \tag{57}$$

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5.3   Spin-orbit Energy and Eigenstates

To correctly use perturbation theory, we need to find eigenstates of $\hat{\mathcal{H}}_s$. However, as we can check $\left[\hat{s}_z, \hat{\mathcal{H}}_s\right] \neq 0$ and $\left[\hat{\ell}_z, \hat{\mathcal{H}}_s\right] \neq 0$, the eigenstates of $\hat{\mathcal{H}}_s$ are not simultaneous eigenstates of $\hat{s}_z$ and $\hat{\ell}_z$.

On the other hand, because there is no external torque, we can consider the **total electron angular momentum**:

$$\hat{\mathbf{j}} = \hat{\boldsymbol{\ell}} + \hat{\mathbf{s}}. \tag{58}$$

We can verify $\left[\hat{j}^2, \hat{\mathcal{H}}_s\right] = \left[\hat{j}_z, \hat{\mathcal{H}}_s\right] = \left[\hat{s}^2, \hat{\mathcal{H}}_s\right] = \left[\hat{\ell}^2, \hat{\mathcal{H}}_s\right] = 0$. The amount of orbital and spin angular momenta is still conserved; it's just the specific components that are not. Therefore, the new set of complete compatible observables should be denoted by

$$|nljm_j\rangle. \tag{59}$$

By the formula

$$\hat{j}^2 = \hat{\mathbf{j}} \cdot \hat{\mathbf{j}} = \hat{\ell}^2 + \hat{s}^2 + 2\hat{\boldsymbol{\ell}} \cdot \hat{\mathbf{s}}, \tag{60}$$

we can rewrite (57) as

$$\hat{\mathcal{H}}_s = \alpha^2 \left(\frac{1}{2}\alpha^2 m_e c^2\right) \beta_{nl} \left(\frac{\hat{j}^2 - \hat{\ell}^2 - \hat{s}^2}{2\hbar^2}\right). \tag{61}$$

Therefore, the energy of a specific state $|nljm_j\rangle$ is given by

$$\delta E_s = \alpha^2 \times 13.6\,\text{eV} \times \beta_{nl} \times \left[\frac{j(j+1) - l(l+1) - s(s+1)}{2}\right]. \tag{62}$$

By the triangular condition (11), we know the value of j:

$$j = 1/2 \qquad \text{if } l = 0$$

$$j = l \pm 1/2 \qquad \text{if } l > 0.$$

When $j = l - 1/2$, there is a slight decrease in energy, while $j = l + 1/2$ corresponds to a slight increase. Loosely speaking, these correspond to the cases when the magnetic moment and field are aligned and anti-aligned ($\hat{\mathcal{H}} = -\hat{\mu} \cdot \mathbf{B}$ is negative when aligned).

In gross structure model, two states of the same n and l share the same energy. In fine structure model, for $l > 0$ the degeneracy is lifted by the spin-orbit interaction.

6 Hydrogen Hyperfine Structure

6.1 Hamiltonian

The hyperfine structure of hydrogen considers, additionally, the nuclear (proton) spin. The spin of a nucleus is described by the angular momentum operator $\hat{\mathbf{I}}$. The associated magnetic moment is

$$\hat{\mu}_I = \frac{g_I \mu_{\mathrm{N}} \hat{\mathbf{I}}}{\hbar} \quad \text{with} \quad \mu_{\mathrm{N}} = \frac{e\hbar}{2m_p} \text{ (nuclear magneton).} \tag{63}$$

The relatively massive proton means that $\dfrac{\mu_{\mathrm{N}}}{\mu_{\mathrm{B}}} \approx \dfrac{1}{2000}$, and the gyromagnetic factor for a single proton is $g_I = 5.6$. Similar to the fine structure, we may write the hyperfine structure Hamiltonian as

$$\hat{\mathcal{H}}_h = A_h \frac{\hat{\mathbf{I}} \cdot \hat{\mathbf{j}}}{\hbar^2} \tag{64}$$

for some factor of A_h. It is proportional to the magnetic field created by the total electron angular momentum.

6.2 Energy and Eigenstates

Similarly, we define the **total atom angular momentum**

$$\hat{\mathbf{f}} = \hat{\mathbf{j}} + \hat{\mathbf{I}}. \tag{65}$$

The complete set of quantum numbers should then be (n, l, j, f, m_f). The first-order correction of energy levels is

$$\delta E_h = A_{nlj} \times \left[\frac{f(f+1) - j(j+1) - I(I+1)}{2} \right], \tag{66}$$

where $A_{nlj} = \langle A_h \rangle$ is called the hyperfine structure constant.

6.3 Estimating the Ground State Hyperfine Structure Constant

The magnetic field inside a uniform sphere of magnetization $\mathbf{M}_0$ is $\dfrac{2}{3}\mu_0 \mathbf{M}_0$. By using the probability density at the origin to approximate, we have

$$\hat{\mathcal{H}}_h = -\hat{\mu}_I \cdot \mathbf{B}_0 = \frac{8g_I}{3} \left(\frac{m_e}{m_p} \right) \alpha^2 \left(\frac{1}{2}\alpha^2 m_e c^2 \right) \frac{\hat{\mathbf{I}} \cdot \hat{\mathbf{s}}}{\hbar^2} = A_{1s} \frac{\hat{\mathbf{I}} \cdot \hat{\mathbf{s}}}{\hbar^2} \tag{67}$$

for the ground state, where we used $|u_{100}|^2$ to calculate $\mathbf{B}_0$. In general, the characteristic energy scale of hyperfine structure is reduced from fine structure by the ratio m_e/m_p. However, actually, the numerical factors are significant, and the difference is not so much.

7 The Zeeman Effect

The Zeeman effect discusses the effect of an external weak magnetic field. The interaction Hamiltonian is therefore

$$\hat{\mathcal{H}}_Z = -\left(\hat{\mu}_l + \hat{\mu}_s + \hat{\mu}_I\right) \cdot \mathbf{B}, \tag{68}$$

for the three magnetic dipoles from electron angular momentum, electron spin, and nuclear spin. We may neglect the contribution from nuclear spin, as it is m_e/m_p times smaller than the electron spin. With $\mathbf{B}$ pointing in z-axis, we have

$$\hat{\mathcal{H}}_Z \approx \mu_{\mathrm{B}} B \left(\frac{2\hat{s}_z}{\hbar} + \frac{\hat{\ell}_z}{\hbar} \right). \tag{69}$$

We won't do any detailed calculations, as it is already vertiginous enough. The main idea here is that the expectation value of the z-component of the atom's total magnetic moment must be proportional to that of the z-component of the total angular momentum:

$$\delta E_Z = g_f \mu_{\mathrm{B}} B m_f, \tag{70}$$

with the state-dependent effective gyromagnetic factor g_f.

The largest static magnetic fields we can generate in labs range from $10 \sim 100\,\mathrm{T}$. On this scale, the Zeeman effect would be larger than either fine or hyperfine structure corrections, so it needs to be treated prior to these two.

To summarize, the Zeeman effect lifts the energy degeneracy in m_f.

Part II

Atom-Light Interaction

8   Introduction

The second part of this course is one chapter more of the unprecedented disaster. I hated EM2 until I meet atomic physics.

The main result is the radiative rate equation. By assuming there are a total of two species (the resonance effect makes this assumption valid), we have the coupled rate equations:

$$
\begin{aligned}
\frac{\mathrm{d}N_2}{\mathrm{d}t} &= \begin{pmatrix} \text{absorption} \\ \text{rate} \end{pmatrix} N_1 - \begin{pmatrix} \text{stimulated} \\ \text{emission rate} \end{pmatrix} N_2 - \begin{pmatrix} \text{spontaneous} \\ \text{emission rate} \end{pmatrix} N_2 \\
\frac{\mathrm{d}N_1}{\mathrm{d}t} &= -\frac{\mathrm{d}N_2}{\mathrm{d}t}.
\end{aligned}
\tag{71}
$$

The second equation is due to the fact that the system is **closed**.

Absorption   Stimulated Emission   Spontaneous Emission
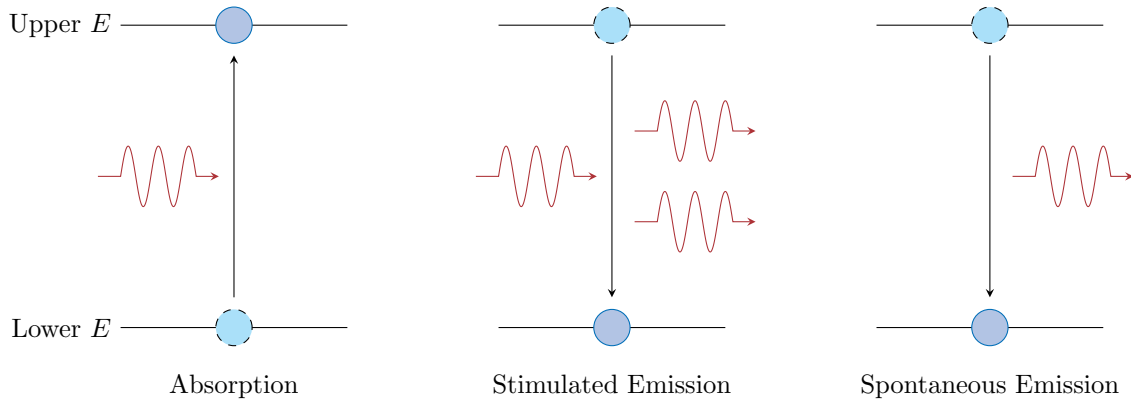
Our original goal was to investigate how atoms respond to light. The result is Rabi oscillations, and the energy goes back and forth between the electron and the field. This corresponds to the processes of absorption and stimulated emission. Also, it is unphysical that an electron sans external interference can stay at high energy state forever, so we introduces spontaneous emission as a damping term of the high energy species.

The three processes mentioned above dictate our study of atom-light interaction.

9 Electric Dipole Hamiltonian

9.1 The Electric Dipole Approximation

Firstly, we construct an electric field in the vicinity of the atom as a traveling plane wave. By defining the zero of external potential to be the case that the electron and proton are both located at the origin, we have

$$U = -W = -\int_0^{\mathbf{r}} q\mathbf{E} \cdot \mathrm{d}\mathbf{s} \,.$$

Typical light wavelength is much larger compared to the size of an atom, so we could safely approximate the electric field to be constant over the region of interest:

$$\mathbf{E}(x,t) = \hat{\mathbf{e}}_z \mathcal{E}_0 \cos(\omega t - kx) \quad \Rightarrow \quad U \approx -q\mathbf{E}(0,t) \cdot \mathbf{r} = -q\mathcal{E}_0 \cos(\omega t)z.$$

In the picture of quantum mechanics, this energy turns into an operator, which implies that we replace z with position operator $\hat{z}$. If we define the **electric dipole operator**

$$\hat{\mathbf{d}} = \sum_i q_i \hat{\mathbf{r}}_i, \tag{72}$$

then we have the electric dipole Hamiltonian

$$\hat{\mathcal{H}}_I = -\mathbf{E} \cdot \hat{\mathbf{d}}. \tag{73}$$

One thing to note is that our electric dipole in electromagnetism points from the negative charge to the positive charge. The case is reversed here.

9.2 Transitions and Selection Rules

Our first order time-independent perturbation theory implies that an eigenstate for the total Hamiltonian should be in the form of

$$\psi_i' = \psi_i + \sum_{j \neq i} \frac{\langle \psi_j | \hat{\mathcal{H}}_I | \psi_i \rangle}{E_i - E_j} \psi_j. \tag{74}$$

This is not the case here, because we're dealing with the time dependent electric fields. Nevertheless, the numerator $\langle \psi_j | \hat{\mathcal{H}}_I | \psi_i \rangle$ describes how $\hat{\mathcal{H}}_I$ connects the state ψ_i to the state ψ_j and is thus very general; it pops up in our later time-dependent calculation.

9.3 Parity Selection Rule

The symmetries of the wavefunctions prohibit some electric dipole transitions. To make a general argument, let's try computing our overlap integral using a coordinate system that has been inverted through the origin, $\mathbf{r}' = -\mathbf{r}$. This suggests

$$\mathbf{r}' = -\mathbf{r} \quad \Rightarrow \quad \begin{cases} (x', y', z') = (-x, -y, -z) \\ (r', \theta', \phi') = (r, \pi - \theta, \phi - \pi). \end{cases} \tag{75}$$

The vector dipole moment, which acts in only spatial coordinates, shouldn't change with a coordinate transformation. Therefore,

$$\langle n'l'm'|\hat{\mathbf{r}}|nlm\rangle = \langle n'l'm'|\hat{\mathbf{r}}|nlm\rangle$$

$$\iint d\mathbf{r}\, d\mathbf{r}' \, \langle n'l'm'|-\mathbf{r}\rangle \, \langle -\mathbf{r}|\hat{\mathbf{r}}|-\mathbf{r}'\rangle \, \langle -\mathbf{r}'|nlm\rangle = \iint d\mathbf{r}\, d\mathbf{r}' \, \langle n'l'm'|\mathbf{r}\rangle \, \langle \mathbf{r}|\hat{\mathbf{r}}|\mathbf{r}'\rangle \, \langle \mathbf{r}'|nlm\rangle$$

$$-\int d\mathbf{r}\, \mathbf{r} \left(\langle n'l'|r'\rangle \, \langle r'|nl\rangle \right) \langle l'm'|\theta', \phi'\rangle \, \langle \theta', \phi'|lm\rangle = \int d\mathbf{r}\, \mathbf{r} \left(\langle n'l'|r\rangle \, \langle r|nl\rangle \right) \langle l'm'|\theta, \phi\rangle \, \langle \theta, \phi|lm\rangle$$

$$\Rightarrow \quad (-1)^{(l+l')} = -1,$$

where the last step follows from the fact that

$$\langle \theta', \phi'|lm\rangle = (-1)^l \, \langle \theta, \phi|lm\rangle. \tag{76}$$

> Hence, we know that electric dipole transition only allows states which satisfies
>
> $$(-1)^{\Delta l} = -1, \tag{77}$$
>
> where $\Delta l = l' - l$. This is called the **parity selection rule**.

9.4 Angular Momentum Selection Rules

The electric dipole Hamiltonian interacts only with spatial coordinates, so the spin states must be compatible to yield a nonzero value. For example, in the gross-structure of hydrogen, we need $m_s = m_{s'}$. In helium (and other multielectron atoms), we need $S = S'$, so the electric dipole transitions can happen among parahelium ($S = 0$) and orthohelium ($S = 1$), but not from one to the other.

We should consider the total angular momentum of the atom and the radiation field together, which must be conserved when the atom's state changes by absorbing or emitting a single photon (spin $= 1$). As a result, the orbital angular momentum l can change by at most 1 when a photon is absorbed or emitted.

Combining this with parity selection rule, only $\Delta l = \pm 1$ is allowed. For fine structure states, we have $\Delta j = 0$ or ± 1. The specific component of angular momentum should also be conserved, so we have $\Delta m_j = 0$ or ± 1. If hyperfine structure is considered, then $\Delta f = 0$ or ± 1, and $\Delta m_f = 0$ or ± 1.

9.5   Higher Order Transitions and Metastable States

When an electric-dipole transition is forbidden due to selection rules, weaker, higher-order transitions become significant. We've so far assumed that the electric field is constant over the region of interest. If variation is allowed, then we have electric quadrupole transition. Also, we should consider the magnetic interaction with the radiation field. This leads to the magnetic dipole transition.

10   Rabi Oscillations

For simplicity, let's begin with only two possible energy eigenstates of $\hat{\mathcal{H}}_0$ ($\hat{\mathcal{H}}_I$ is treated as the perturbation). We define the resonant frequency of the two atomic states:

$$\omega_0 = \frac{E_2 - E_1}{\hbar}. \tag{78}$$

The sum $(E_2 + E_1)/\hbar$ varies with a constant shift in the potential energy and thus has no physical significance.

Any wavefunction in the system should be represented as a linear combination of the two possible eigenfunctions. With insight, we write

$$\psi(t) = \left[c_1(t)\exp\left(-\frac{iE_1 t}{\hbar}\right)\right]\psi_1 + \left[c_2(t)\exp\left(-\frac{iE_2 t}{\hbar}\right)\right]\psi_2. \tag{79}$$

We then plug this expression into the Schrödinger equation:

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\psi(t) = \left(\hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_I\right)\psi(t) \tag{80}$$

By taking inner product with the orthonormal states and noting from our erstwhile discussions that $\langle\psi_i|\hat{\mathcal{H}}_I|\psi_i\rangle = 0$, we get

$$\begin{aligned}
i\hbar\frac{\mathrm{d}c_1}{\mathrm{d}t} &= c_2(t)\mathrm{e}^{-i\omega_0 t}\langle\psi_1|\hat{\mathcal{H}}_I|\psi_2\rangle \\
i\hbar\frac{\mathrm{d}c_2}{\mathrm{d}t} &= c_1(t)\mathrm{e}^{i\omega_0 t}\langle\psi_2|\hat{\mathcal{H}}_I|\psi_1\rangle.
\end{aligned} \tag{81}$$

Recall that

$$\hat{\mathcal{H}}_I = -\mathcal{E}_0\cos(\omega t)\hat{d}_z = e\mathcal{E}_0\cos(\omega t)\hat{z}. \tag{82}$$

If we define the **Rabi frequency** $\Omega \in \mathbb{R}$,

$$\Omega = -\frac{\mathcal{E}_0}{\hbar}\langle\psi_1|\hat{d}_z|\psi_2\rangle, \tag{83}$$

we may expand $\cos(\omega t)$ in (81). The oscillation by the argument of $\omega + \omega_0$ has no time-averaged effect, so we could safely focus on only the difference part (rotating-wave approximation):

$$\begin{aligned}
\frac{\mathrm{d}c_1}{\mathrm{d}t} &= -i\frac{\Omega}{2}\mathrm{e}^{i\delta t}c_2(t) \\
\frac{\mathrm{d}c_2}{\mathrm{d}t} &= -i\frac{\Omega}{2}\mathrm{e}^{-i\delta t}c_1(t),
\end{aligned} \tag{84}$$

where $\delta = \omega - \omega_0$. By taking the derivative with respect to the second equation, we get the second order

differential equation with constant coefficients. Therefore,

$$P_2(t) = |c_2(t)|^2 = \frac{\Omega^2}{\Omega^2 + \delta^2} \sin^2\left(\frac{\sqrt{\Omega^2 + \delta^2}}{2} t\right). \qquad (85)$$