The hydrogen fine structure.

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Postulates and symmetries, a brief review.

- Physical states are represented as vectors in a Hilbert space.
- Observable quantities are represented by Hermitian operators acting on the states of the Hilbert space. $\left\langle \phi \left| A^\dagger \right| \psi \right\rangle = \langle \psi | A | \phi \rangle^*$, $\quad (A^\dagger)_{ij} = a^*_{ji}$, .
- The measurement of the property represented by the observable A gives one of its eigenvalues (a) and, after the measurement, the state vector of the system is the eigenstate of A corresponding to the eigenvalue obtained, ϕ_a.
- The probability of obtaining that particular value is (for discrete spectra)

$$P(a) = \frac{|\langle \phi_a | \Psi \rangle|^2}{\langle \phi_a | \phi_a \rangle \langle \Psi | \Psi \rangle}. \tag{1}$$

- The state vector of the system evolves in time according to the Schrödinger equation,

$$i\hbar \frac{\mathrm{d}\Psi(t)}{\mathrm{d}t} = \mathcal{H}\Psi(t) \tag{2}$$

where the hermitian operator $\mathcal{H}$ is the Hamiltonian of the system and represents its total energy.

Symmetries in quantum mechanics are represented by unitary linear operators, $U^\dagger = U^{-1}$. They keep transition probabilities invariant.

$$\langle \Psi_2 \,|\, \Psi_1 \rangle \;\longrightarrow\; \langle \Psi_2' \,|\, \Psi_1' \rangle = \langle U\Psi_2 \,|\, U\Psi_1 \rangle = \langle \Psi_2 \,|\, U^\dagger U \Psi_1 \rangle = \langle \Psi_2 \,|\, \Psi_1 \rangle . \quad (3)$$

For operators that can be arbitrarily close to the identity operator, $\mathbf{1}$,

$$U_\epsilon = \mathbf{1} + i\epsilon T + O(\epsilon^2), \quad (4)$$

where ϵ is an arbitrary real infinitesimal number, and T is some operator which does not depend on ϵ.

To first order in ϵ, the unitary condition is

$$U_\epsilon^\dagger U_\epsilon = \Big(\mathbf{1} - i\epsilon T^\dagger + O(\epsilon^2)\Big)\Big(\mathbf{1} + i\epsilon T + O(\epsilon^2)\Big) = \mathbf{1} + i\epsilon(T - T^\dagger) + O(\epsilon^2) = \mathbf{1},$$

$$\text{so} \qquad T = T^\dagger . \quad (5)$$

Hermitian operators arise naturally associated to infinitesimal symmetries.

Take now $\epsilon = \theta/n$, where θ is an n-independent finite parameter. Then

$$\lim_{n\to\infty}\left(\mathbf{1}+\frac{i\theta T}{n}\right)^n = e^{i\theta T} = \sum_{n=0}^{\infty}\frac{(i\theta T)^n}{n!} = U(\theta). \tag{6}$$

The operator T is known as the *generator of the symmetry*. Many of the operators representing observables in quantum mechanics are the generators of symmetries.

Under a symmetry transformation, $\Psi' = U\Psi$, the expectation value of any observable A undergoes the following transformation

$$\langle\Psi\,|\,A\Psi\rangle \longrightarrow \langle U\Psi\,|\,AU\Psi\rangle = \left\langle\Psi\,\middle|\,U^{-1}AU\Psi\right\rangle. \tag{7}$$

The transformation properties of the matrix elements can then be found by transforming the observables as

$$A \longrightarrow A' = U^{-1}AU. \tag{8}$$

If we take $U_\epsilon = \mathbf{1} + i\epsilon T + O(\epsilon^2)$, then the operator A is transformed as

$$A \longrightarrow A' = U_\epsilon^{-1}AU_\epsilon = (\mathbf{1}-i\epsilon T)A(\mathbf{1}+i\epsilon T) = A + i\epsilon AT - i\epsilon TA = A - i\epsilon[T,A].$$

The effect of infinitesimal symmetry transformations on any operator can be expressed through the commutation relations of the symmetry generator with that operator.

Time translations.

The physical results obtained from the state vectors $\Psi(t)$ and $\Psi(t+\tau)$, where τ is an arbitrary time amount, should be physically equivalent for isolated systems. This means there should be some linear unitary operator $U(\tau)$ such that

$$U(\tau)\Psi(t) = \Psi(t+\tau). \tag{9}$$

Since τ is a continuous variable that can be arbitrarily small, it must be possible to express $U(\tau)$ as

$$U(\tau) = e^{i\tau T}$$

Instead of the Hermitian operator T, we may write $T = -\mathcal{H}/\hbar$, so that

$$U(\tau) = \exp\left(-\frac{i\mathcal{H}\tau}{\hbar}\right) \tag{10}$$

This can be taken as the **definition** of the Hamiltonian $\mathcal{H}$.

By setting $t = 0$ in $U(\tau)\Psi(t) = \Psi(t+\tau)$, and replacing τ with t, we have

$$U(t)\Psi(0) = \exp\left(-\frac{i\mathcal{H}t}{\hbar}\right)\Psi(0) = \Psi(t).$$

$$\Psi(t) = \exp\left(-\frac{i\mathcal{H}t}{\hbar}\right)\Psi(0). \tag{11}$$

Taking the time derivative we find

$$\frac{\mathrm{d}\Psi(t)}{\mathrm{d}t} = -\frac{i\mathcal{H}}{\hbar}\exp\left(-\frac{i\mathcal{H}t}{\hbar}\right)\Psi(0) = \frac{1}{i\hbar}\mathcal{H}\Psi(t). \tag{12}$$

$$\mathcal{H}\Psi(t) = i\hbar\frac{\mathrm{d}\Psi(t)}{\mathrm{d}t} \tag{13}$$

This is the general version of the time-dependent Schrödinger equation.

Time translation invariance leads to the energy conservation law, which applies only to isolated systems.

Space translations.

Under a translation by an arbitrary three-vector $\mathbf{a}$, the expectation value of any particle coordinate $\mathbf{X}$ is transformed to $\mathbf{X} + \mathbf{a}$.

$$U^{-1}(\mathbf{a})\, \mathbf{X}\, U(\mathbf{a}) \;=\; \mathbf{X} + \mathbf{a}. \tag{14}$$

For $\mathbf{a}$ infinitesimal, U must take the form $U_\epsilon = \mathbf{1} + i\epsilon T + O(\epsilon^2)$.

We use now the Hermitian operator $-\mathbf{P}/\hbar$ instead of T, and the three-vector parameter $\mathbf{a}$ instead of ϵ, to write

$$U(\mathbf{a}) = \mathbf{1} - \frac{i}{\hbar}\mathbf{P}\cdot\mathbf{a} + O(\mathbf{a}^2). \tag{15}$$

This can be taken as the **definition** of the momentum operator, $\mathbf{P} = (P_1, P_2, P_3)$.

Insert the infinitesimal expression for U in equation (14). To first order in $\mathbf{a}$:

$$\left(\mathbf{1} + \frac{i}{\hbar}\mathbf{P}\cdot\mathbf{a}\right)\mathbf{X}\left(\mathbf{1} - \frac{i}{\hbar}\mathbf{P}\cdot\mathbf{a}\right) = \mathbf{X} - \frac{i}{\hbar}\mathbf{X}\cdot(\mathbf{P}\cdot\mathbf{a}) + \frac{i}{\hbar}(\mathbf{P}\cdot\mathbf{a})\cdot\mathbf{X}$$

$$= \mathbf{X} + \frac{i}{\hbar}[(\mathbf{P}\cdot\mathbf{a}), \mathbf{X}] = \mathbf{X} + \mathbf{a} \quad \Longrightarrow \quad \frac{i}{\hbar}[(\mathbf{P}\cdot\mathbf{a}), \mathbf{X}] = \mathbf{a}.$$

We conclude that the following relation must be satisfied for any infinitesimal three-vector $\mathbf{a}$

$$\frac{i}{\hbar}[(\mathbf{P}\cdot\mathbf{a}),\mathbf{X}]=\mathbf{a}, \qquad [\mathbf{X},(\mathbf{P}\cdot\mathbf{a})]=i\hbar\mathbf{a}. \tag{16}$$

Taking now the first component of the $\mathbf{X}$ operator, X_1, and a translation along the X_1–axis, we have

$$[X_1, P_1 a_1] = i\hbar a_1. \tag{17}$$

This relation holds for any a_1 only if we have $[X_1, P_1] = i\hbar$.

Likewise, we have $[X_2, P_2] = i\hbar$ and $[X_3, P_3] = i\hbar$.

In a more compact form,

$$[X_i, P_j] = i\hbar\delta_{ij}. \tag{18}$$

A translation by a vector $\mathbf{a}$ followed by a translation by a vector $\mathbf{b}$ gives the same result as a translation by $\mathbf{b}$ followed by a translation by $\mathbf{a}$, therefore

$$U(\mathbf{b})U(\mathbf{a}) = U(\mathbf{a})U(\mathbf{b}). \tag{19}$$

From this follows that $$[P_i, P_j] = 0. \tag{20}$$

Because they commute, we can find a complete set of eigenvectors of all three components of momentum, so we can write for an arbitrary finite translation

$$U(\mathbf{a}) = \exp\left(-i\frac{\mathbf{P}\cdot\mathbf{a}}{\hbar}\right) \tag{21}$$

Let $|\Phi_0\rangle$ be a one–particle state with a definite position at the origin.

This is an eigenstate of the position operator $\mathbf{X}$ with eigenvalue zero.

We can form an eigenstate with definite position $\mathbf{x}$ using the space translation operator,

$$|\Phi_{\mathbf{x}}\rangle \equiv U(\mathbf{X})\,|\Phi_0\rangle\,. \tag{22}$$

Of course, the position operator acts on this eigenstate according to

$$\mathbf{X}\,|\Phi_{\mathbf{x}}\rangle = \mathbf{x}\,|\Phi_{\mathbf{x}}\rangle\,. \tag{23}$$

Any state $|\psi\rangle$ can be expanded in terms of the position eigenstates as

$$|\psi\rangle = \sum C_{\mathbf{x}}\,|\Phi_{\mathbf{x}}\rangle \quad\longrightarrow\quad |\psi\rangle = \int \mathrm{d}^3\mathbf{x}\;|\Phi_{\mathbf{x}}\rangle\overbrace{\langle\Phi_{\mathbf{x}}\,|\,\psi\rangle}^{\psi(\mathbf{x})} = \int \mathrm{d}^3\mathbf{x}\;\psi(\mathbf{x})\;|\Phi_{\mathbf{x}}\rangle\,, \tag{24}$$

where $\psi(\mathbf{x}) = \langle \Phi_{\mathbf{x}} \,|\, \psi \rangle$ is the state wave function in the position representation, and the wave function of the position eigenstate $|\Phi_{\mathbf{x_0}}\rangle$ itself is

$$\langle \Phi_{\mathbf{x}} \,|\, \Phi_{\mathbf{x_0}} \rangle = \delta^3(\mathbf{x} - \mathbf{x_0}).$$

Since this function is zero everywhere except at $\mathbf{x} = \mathbf{x_0}$, we obviously have

$$\mathbf{X}\,|\Phi_{\mathbf{x_0}}\rangle = \mathbf{x_0}\,|\Phi_{\mathbf{x_0}}\rangle.$$

A translation by an amount $\mathbf{a}$ transforms $|\Phi_{\mathbf{x}}\rangle$ into $U(\mathbf{a})\,|\Phi_{\mathbf{x}}\rangle = |\Phi_{\mathbf{x+a}}\rangle$.

For an arbitrary state $|\psi\rangle$ we have then

$$\begin{aligned} U(\mathbf{a})\,|\psi\rangle = U(\mathbf{a}) \int \mathrm{d}^3\mathbf{x}\; \psi(\mathbf{x})\; |\Phi_{\mathbf{x}}\rangle = \int \mathrm{d}^3\mathbf{x}\; \psi(\mathbf{x})\; U(\mathbf{a})\,|\Phi_{\mathbf{x}}\rangle \\ = \int \mathrm{d}^3\mathbf{x}\; \psi(\mathbf{x})\,|\Phi_{\mathbf{x+a}}\rangle = \int \mathrm{d}^3\mathbf{x}'\; \psi(\mathbf{x}' - \mathbf{a})\; |\Phi_{\mathbf{x}'}\rangle\,. \end{aligned} \tag{25}$$

In the last step we have just performed the change of variable $\mathbf{x} + \mathbf{a} \to \mathbf{x}'$.

Hence, the wave function transforms under a translation as.

$$U(\mathbf{a})\psi(\mathbf{x}) = \psi'(\mathbf{x}) = \psi(\mathbf{x}-\mathbf{a}). \tag{26}$$

For $|\mathbf{a}|$ infinitesimal we may Taylor expand $\psi(\mathbf{x}-\mathbf{a})$ and neglect everything beyond first order,

$$\psi(\mathbf{x}-\mathbf{a}) \approx \psi(\mathbf{x}) - \boldsymbol{\nabla}\psi(\mathbf{x})\cdot\mathbf{a}. \tag{27}$$

On the other hand, for such an infinitesimal translation the unitary operator can be written as $U(\mathbf{a}) \approx 1 - \frac{i}{\hbar}\mathbf{P}\cdot\mathbf{a}$. Therefore

$$\langle \Phi_{\mathbf{x}} \,|\, U(a) \,|\, \psi\rangle = \langle \Phi_{\mathbf{x}} \,|\, \psi\rangle - \frac{i}{\hbar}\langle \Phi_{\mathbf{x}} \,|\, \mathbf{P} \,|\, \psi\rangle \cdot \mathbf{a} = \psi(\mathbf{x}) - \frac{i}{\hbar}\langle \Phi_{\mathbf{x}} \,|\, \mathbf{P} \,|\, \psi\rangle \cdot \mathbf{a}. \tag{28}$$

Remember that $\mathbf{a}$ is just a *fixed* three-vector parameter.

Equating (27) to (28) we get

$$\frac{i}{\hbar}\langle \Phi_{\mathbf{x}} \,|\, \mathbf{P} \,|\, \psi\rangle = \boldsymbol{\nabla}\psi(\mathbf{x}). \tag{29}$$

In other words, the momentum operator acts on the wavefunctions as

$$\mathbf{P}\psi(\mathbf{x}) = -i\hbar\boldsymbol{\nabla}\psi(\mathbf{x}). \tag{30}$$

It can be seen that space translation invariance leads to the momentum conservation law.

Note that the representation of the momentum operator as $\mathbf{P} = -i\hbar\boldsymbol{\nabla}$, as well as the commutation relations $[X_i, P_j] = i\hbar\delta_{ij}$, are not postulates. They both follow from the fundamental properties of spatial translations.

In fact, they are closely related in the sense that the representation $\mathbf{P} = -i\hbar\boldsymbol{\nabla}$ can also be inferred from the commutation relations, as you will see in one of the problems.

Rotations and angular momentum.

Invariance under rotations leads to the existence of a conserved angular momentum three–vector observable, **J**.

A rotation in the ordinary three-dimensional space is a linear transformation $x_i' = \sum_j R_{ij} x_j$ of the Cartesian coordinates x_i that leaves invariant the scalar product $\mathbf{xy} = \sum_i x_i y_i$.

$$\sum_i x_i' x_i' = \sum_i \left(\sum_j R_{ij} x_j \right) \left(\sum_k R_{ik} x_k \right) = \sum_{j,k} \left(\sum_i R_{ij} R_{ik} \right) x_j x_k = \sum_j x_j x_j .$$

This implies

$$\sum_i R_{ij} R_{ik} = \delta_{jk}, \qquad \text{or} \qquad R^T R = 1,$$

where R^T is the transpose of a matrix and 1 the unit matrix, $[1]_{jk} = \delta_{jk}$.

Space inversions, $\mathbf{x} \to -\mathbf{x}$, satisfy also the relation $R^T R = 1$. We will work only with rotations and demand $\det(R) = +1$.

It is **very important** to note that the operator R acts on the ordinary three-dimensional space, not on the Hilbert space.

A rotation induces a unitary transformation on the Hilbert space of physical states, $\Psi' = U(R)\Psi$, such that the following relation holds

$$U(R_2)U(R_1) = U(R_2 R_1). \tag{31}$$

On any operator $\mathbf{V}$ representing a **vector** observable, $U(R)$ must induce the following rotation

$$U^{-1}(R)V_i U(R) = \sum_j R_{ij} V_j. \tag{32}$$

It is not difficult to prove that the most general unitary operator for infinitesimal rotations in three dimensions can be written as

$$U(1+\omega) = \mathbf{I} - \frac{i}{\hbar}\mathbf{J}\cdot\boldsymbol{\omega} + \mathbf{O}(\omega^2), \tag{33}$$

where $\mathbf{J} = (J_1, J_2, J_3)$ is a set of Hermitian operators and the factor $1/\hbar$ is inserted in order to give J_i the dimensions of $\hbar$.

This is a rotation by an infinitesimal angle $|\boldsymbol{\omega}|$ around an axis in the direction of the vector $\boldsymbol{\omega}$. The three–vector operator $\mathbf{J}$ is the generator of spatial rotations.

This can be taken as the **definition of angular momentum** in quantum mechanics.

The unitary operator for an arbitrary rotation, not necessarily infinitesimal, is

$$U(R) = \exp\left(-\frac{i}{\hbar}\mathbf{J}\cdot\boldsymbol{\omega}\right) \tag{34}$$

The commutation relations between the components of $\mathbf{J}$ and any other three–vector operator $\mathbf{V}$ are

$$[J_i, V_j] = i\hbar\sum_k \epsilon_{ijk} V_k. \tag{35}$$

A vector operator can be defined as an operator that verifies the previous commutation relations with the generators of spatial rotations.

A scalar operator K commutes with those generators, $[J_i, K] = 0$.
Since $\mathbf{J}$ is itself a vector, it satisfies

$$[J_i, J_j] = i\hbar\sum_k \epsilon_{ijk} J_k. \tag{36}$$

From the previous commutation relations one can work out the eigenvalues of $\mathbf{J}^2$ and J_3, and the action of $\mathbf{J}$ on a multiplet of eigenstates of these operators.

Denoting the eigenstates by $|jm\rangle$, the eigenvalue equations are

$$J_3 |jm\rangle = \hbar m |jm\rangle ; \qquad \mathbf{J}^2 |jm\rangle = \hbar^2 j(j+1) |jm\rangle ; \qquad m = -j, -j+1 \ldots + j. \tag{37}$$

We have also

$$\left(J_1 \pm i J_2\right) |jm\rangle = J_\pm |jm\rangle = \hbar \sqrt{j(j+1) - m(m \pm 1)} \; |jm \pm 1\rangle . \tag{38}$$

By carefully studying how the unitary operator $U(R)$ acts on the wave functions in the coordinate representation, $\Psi(\mathbf{X})$, it can be seen that the total angular momentum operator $\mathbf{J}$ acts on $\Psi(\mathbf{X})$ as

$$\mathbf{J}\Psi(\mathbf{X}) = -i\hbar(\mathbf{X} \times \boldsymbol{\nabla})\Psi(\mathbf{X}). \tag{39}$$

Defining the **orbital angular momentum** operator as $\mathbf{L} \equiv \mathbf{X} \times \mathbf{P}$, the previous relation becomes

$$\mathbf{J}\Psi(\mathbf{X}) = \mathbf{L}\Psi(\mathbf{X}). \tag{40}$$

This says that $\mathbf{J}$ acts on $\Psi(\mathbf{X})$ like the $\mathbf{L}$ operator, but **it does not say** that $\mathbf{J} = \mathbf{L}$, because $\mathbf{J}$ may have a term which does not act on space wave functions,

$$\mathbf{J}\Psi(\mathbf{X}) = (\mathbf{L} + \mathbf{S})\,\Psi(\mathbf{X}) = \mathbf{L}\Psi(\mathbf{X}). \tag{41}$$

By direct computation it is easy to see that $\mathbf{L}$ satisfies the same commutation relations as $\mathbf{J}$,

$$[L_i, L_j] = i\hbar \sum_k \epsilon_{ijk} L_k. \tag{42}$$

The generator of rotations is $\mathbf{J}$, not $\mathbf{L}$, and since $\mathbf{L}$ is a vector, it must satisfy the same commutation relations with $\mathbf{J}$ as any other vector. Therefore

$$[J_i, L_j] = i\hbar \sum_k \epsilon_{ijk} L_k. \tag{43}$$

If we now **define** an operator $\mathbf{S} \equiv \mathbf{J} - \mathbf{L}$, so that

$$\mathbf{J} = \mathbf{L} + \mathbf{S}, \tag{44}$$

then by subtracting (42) from (43) we find

$$[J_i, L_j] - [L_i, L_j] = i\hbar \sum_k \epsilon_{ijk} L_k - i\hbar \sum_k \epsilon_{ijk} L_k = 0.$$

But

$$[J_i, L_j] - [L_i, L_j] = [L_i + S_i, L_j] - [L_i, L_j] = [L_i, L_j] + [S_i, L_j] - [L_i, L_j] = [S_i, L_j].$$

Therefore

$$[S_i, L_j] = 0. \tag{45}$$

From equations (45), (44), (42) and (36) it is possible to infer that

$$[S_i, S_j] = i\hbar \sum_k \epsilon_{ijk} S_k. \tag{46}$$

The operator **S** acts as a new kind of angular momentum. It may be thought of as an internal property of the particle, called **spin**. **The spin is not constructed from the position and momentum operators, and commutes with them**. Direct calculation gives

$$[L_i, X_j] = i\hbar \sum_k \epsilon_{ijk} X_k, \qquad [L_i, P_j] = i\hbar \sum_k \epsilon_{ijk} P_k. \tag{47}$$

On the other hand, as every vector operator, **X** and **P** must satisfy

$$[J_i, X_j] = i\hbar \sum_k \epsilon_{ijk} X_k, \qquad [J_i, P_j] = i\hbar \sum_k \epsilon_{ijk} P_k. \tag{48}$$

The difference between equations (47) and (48) gives $[S_i, X_j] = [S_i, P_j] = 0$.

We have seen that the **ladder operators**, defined as $J_\pm = (J_1 \pm iJ_2)$, satisfy

$$J_\pm \, |jm\rangle = \hbar\sqrt{j(j+1) - m(m\pm 1)} \; |j(m\pm 1)\rangle.$$

$$J_1 = \frac{1}{2}(J_+ + J_-), \qquad J_2 = \frac{1}{2i}(J_+ - J_-).$$

It is usual to define, by analogy with the spherical harmonics $Y_1^m(\theta,\varphi)$, the **spherical components** of a general angular momentum **J** as

$$J_{+1} = -\frac{1}{\sqrt{2}}(J_x + iJ_y), \qquad J_0 = J_z, \qquad J_{-1} = \frac{1}{\sqrt{2}}(J_x - iJ_y). \tag{49}$$

$$J_x = -\frac{1}{\sqrt{2}}(J_{+1} - J_{-1}), \qquad J_z = J_0, \qquad J_y = \frac{i}{\sqrt{2}}(J_{+1} + J_{-1}). \tag{50}$$

The following relations are verified,

$$[J_0, J_{\pm 1}] = \pm J_{\pm 1}, \quad [J_{+1}, J_{-1}] = -J_0, \quad J^2 = J_x^2 + J_y^2 + J_z^2. \tag{51}$$

$$J^2 = -J_{+1}J_{-1} + J_0^2 - J_{-1}J_{+1} = \sum_q (-1)^q J_q J_{-q}$$

$$= -2J_{+1}J_{-1} + J_0(J_0 - 1) = -2J_{-1}J_{+1} + J_0(J_0 + 1) \tag{52}$$

J^2 commutes with all the rectangular and spherical components of $\mathbf{J}$

$$[J^2, J_\mu] = 0.$$

The action of the $J_{\pm 1}$ operators on the angular momentum eigenstates is

$$J_{\pm 1} \left| jm \right\rangle = \mp \hbar \sqrt{\tfrac{1}{2} \left[j(j+1) - m(m \pm 1) \right]} \left| j(m \pm 1) \right\rangle . \tag{53}$$

The spin-j representation matrix elements of the angular momentum operators can be computed using the following relations,

$$\left\langle jm' \left| J_3^{(j)} \right| jm \right\rangle = \left[J_3^{(j)} \right]_{m'm} = m\hbar\, \delta_{m'm}.$$

$$\left\langle jm' \left| J_1^{(j)} \right| jm \right\rangle = \left[J_1^{(j)} \right]_{m'm} = \frac{1}{2} \left(\left[J_+^{(j)} \right]_{m'm} + \left[J_-^{(j)} \right]_{m'm} \right).$$

$$\left\langle jm' \left| J_2^{(j)} \right| jm \right\rangle = \left[J_2^{(j)} \right]_{m'm} = \frac{1}{2i} \left(\left[J_+^{(j)} \right]_{m'm} - \left[J_-^{(j)} \right]_{m'm} \right).$$

$$\left\langle jm' \left| J_+^{(j)} \right| jm \right\rangle = \left[J_+^{(j)} \right]_{m'm} = \hbar \sqrt{j(j+1) - m(m+1)}\, \delta_{m',m+1}.$$

$$\left\langle jm' \left| J_-^{(j)} \right| jm \right\rangle = \left[J_-^{(j)} \right]_{m'm} = \hbar \sqrt{j(j+1) - m(m-1)}\, \delta_{m',m-1}.$$

Angular momentum operators for $j = 1/2, 1, 3/2$.

To be specific, it is useful to display the angular momentum representation for the three lowest dimensions.

The spin-j representation of the angular momentum operators for $j = 1/2$ is

$$J_3^{(1/2)} = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad J_1^{(1/2)} = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad J_2^{(1/2)} = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix},$$

$$J_1^{(1/2)} = \frac{\hbar}{2}\sigma_1, \quad J_2^{(1/2)} = \frac{\hbar}{2}\sigma_2, \quad J_3^{(1/2)} = \frac{\hbar}{2}\sigma_3,$$

where σ_1, σ_2 and σ_3 are the Pauli matrices

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

The basis states are

$$|1/2, 1/2\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \quad |1/2, -1/2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

The spin-j representation of the angular momentum operators for $j = 1$ is

$$J_3^{(1)} = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}; \quad J_1^{(1)} = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}; \quad J_2^{(1)} = \frac{i\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}$$

The basis states are

$$|1,1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}; \quad |1,0\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}; \quad |1,-1\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}.$$

The spin-j representation of the angular momentum operators for $j = 3/2$ is

$$J_3^{(3/2)} = \hbar \begin{pmatrix} 3/2 & 0 & 0 & 0 \\ 0 & 1/2 & 0 & 0 \\ 0 & 0 & -1/2 & 0 \\ 0 & 0 & 0 & -3/2 \end{pmatrix}; \quad J_1^{(3/2)} = \frac{\hbar}{2} \begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}$$

$$J_2^{(3/2)} = \frac{\hbar}{2i}\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 2 & 0 \\ 0 & -2 & 0 & \sqrt{3} \\ 0 & 0 & -\sqrt{3} & 0 \end{pmatrix}.$$

The basis states are

$$\left|\frac{3}{2},\frac{3}{2}\right\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}; \quad \left|\frac{3}{2},\frac{1}{2}\right\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix};$$

$$\left|\frac{3}{2},\frac{-1}{2}\right\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}; \quad \left|\frac{3}{2},\frac{-3}{2}\right\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}.$$

Clebsch–Gordan coefficients.

Two systems with angular momentum $\mathbf{J}_1$ and $\mathbf{J}_2$ can be considered together as a global system with total angular momentum $\mathbf{J}_3 = \mathbf{J}_1 + \mathbf{J}_2$.

Two different basis states of this third system can be written as $|j_1 j_2 j_3 m_3\rangle$ and $|j_1 j_2 m_1 m_2\rangle$.

Using the completeness relation of the states $|j_1 j_2 m_1 m_2\rangle$ we may write

$$|j_1 j_2 j_3 m_3\rangle = \sum_{m_1 m_2} |j_1 j_2 m_1 m_2\rangle \underbrace{\langle j_1 j_2 m_1 m_2 \,|\, j_1 j_2 j_3 m_3\rangle}_{\mathrm{CG}} . \tag{54}$$

The special matrix elements $\langle j_1 j_2 m_1 m_2 \,|\, j_1 j_2 j_3 m_3\rangle$ are called Clebsch-Gordan coefficients. They can be all chosen to be real, so we can also write

$$|j_1 j_2 j_3 m_3\rangle = \sum_{m_1 m_2} \langle j_1 j_2 j_3 m_3 | j_1 j_2 m_1 m_2\rangle \, |j_1 j_2 m_1 m_2\rangle \,, \tag{55}$$

with the inverse relations

$$|j_1 j_2 m_1 m_2\rangle = \sum_{j_3 m_3} \langle j_1 j_2 j_3 m_3 | j_1 j_2 m_1 m_2\rangle \, |j_1 j_2 j_3 m_3\rangle \,. \tag{56}$$

An alternative notation is,

$$\Psi^{m_3}_{j_1 j_2 j_3} = \sum_{m_1 m_2} C_{j_1 j_2}(j_3 m_3; m_1 m_2)\, \Psi^{m_1 m_2}_{j_1 j_2}, \tag{57}$$

with the inverse relations

$$\Psi^{m_1 m_2}_{j_1 j_2} = \sum_{j_3 m_3} C_{j_1 j_2}(j_3 m_3; m_1 m_2)\, \Psi^{m_3}_{j_1 j_2 j_3}. \tag{58}$$

Instead of using the Clebsch-Gordan coefficients to construct states of total angular momentum $\mathbf{J_3}$ from states with individual angular momenta $\mathbf{J_1}$ and $\mathbf{J_2}$, it is possible to use these coefficients to construct a state Ψ of total angular momentum zero from states $\Psi^{m_1 m_2 m_3}_{j_1 j_2 j_3}$ with *three* individual angular momenta:

$$\Psi = \sum_{m_1 m_2 m_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \Psi^{m_1 m_2 m_3}_{j_1 j_2 j_3}. \tag{59}$$

The coefficients multiplying the states $\Psi^{m_3 m_1 m_2}_{j_3 j_1 j_2}$ are called $3j$ symbols, and are related to the CG coefficients by

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \frac{(-1)^{j_1 - j_2 - m_3}}{\sqrt{2j_3 + 1}} \langle j_1 j_2 m_1 m_2 \,|\, j_1 j_2 j_3 - m_3 \rangle \tag{60}$$

The Wigner-Eckart theorem.

Let $|\Phi_j^m\rangle$ be eigenstates of angular momentum with eigenvalues $j(j+1)\hbar^2$ and $m_j\hbar$ for J^2 and J_3, respectively. Recall that

$$(J_1 \pm iJ_2)\left|\Phi_j^m\right\rangle = \hbar\sqrt{j(j+1)-m(m\pm1)}\left|\Phi_j^{m\pm1}\right\rangle$$

$$(J_1 - iJ_2)\left|\Phi_j^{m+1}\right\rangle = \hbar\sqrt{j(j+1)-m(m+1)}\left|\Phi_j^{m}\right\rangle$$

Let $|\Psi_j^m\rangle$ be another set of angular momentum eigenstates. We can write

$$\begin{aligned}\hbar\sqrt{j(j+1)-m(m+1)}\left\langle\Phi_j^{m+1}\middle|\Psi_j^{m+1}\right\rangle &= \left\langle\Phi_j^{m+1}\middle|(J_1+iJ_2)\Psi_j^m\right\rangle \\ &= \left\langle(J_1-iJ_2)\Phi_j^{m+1}\middle|\Psi_j^m\right\rangle = \hbar\sqrt{j(j+1)-m(m+1)}\left\langle\Phi_j^m\middle|\Psi_j^m\right\rangle.\end{aligned}$$

Therefore

$$\left\langle\Phi_j^{m+1}\middle|\Psi_j^{m+1}\right\rangle = \left\langle\Phi_j^m\middle|\Psi_j^m\right\rangle. \tag{61}$$

This shows that the quantity $\left\langle\Phi_j^m\middle|\Psi_j^m\right\rangle$ is independent of m.

Note that any such matrix element with unequal values of j and m vanishes.

$$\left\langle \Phi_{j_3}^{m_3} \,\middle|\, \Psi_{j_2}^{m_2} \right\rangle = 0, \quad \text{unless} \quad j_2 = j_3 \quad \text{and} \quad m_2 = m_3. \tag{62}$$

An irreducible tensor operator of rank j is a set of $2j+1$ operators, O_j^m, with $m = -j, -j+1, \ldots, +j$, such that the commutators of the rotation generators with these operators are

$$[J_3, O_j^m] = \hbar m \, O_j^m. \tag{63}$$

$$[J_1 \pm i J_2, O_j^m] = \hbar \sqrt{j(j+1) - m(m \pm 1)} \, O_j^{m \pm 1}. \tag{64}$$

It is also said that the operators O_j^m have spin j. Examples of irreducible tensor operators are the spherical harmonics. The previous commutation relations can also be written as

$$[J_i, O_j^m] = \sum_{m'} \left[J_i^{(j)} \right]_{m'm} O_j^{m'}, \qquad \text{with } i = 1, 2, 3. \tag{65}$$

These three scalar relations are contained in the following vector one

$$[\mathbf{J}, O_j^m] = \sum_{m'} \left[\mathbf{J}^{(j)} \right]_{m'm} O_j^{m'}, \tag{66}$$

where $\left[\mathbf{J}^{(j)}\right]_{m'm}$ is a matrix element of the spin-j representation of the angular momentum operators. The explicit matrix elements are

$$\left[J_3^{(j)}\right]_{m'm} \equiv \hbar m \delta_{m'm}, \tag{67}$$

$$\left[J_1^{(j)}\right]_{m'm} \pm i \left[J_2^{(j)}\right]_{m'm} \equiv \hbar \sqrt{j(j+1) - m(m\pm 1)}\, \delta_{m',m\pm 1}. \tag{68}$$

The Wigner-Eckart theorem states that

$$\left\langle \Phi^{m_3}_{j_3} \middle| O^{m_1}_{j_1} \middle| \Psi^{m_2}_{j_2} \right\rangle = \frac{1}{2j_3+1} \left\langle j_1 j_2 m_1 m_2 \,|\, j_1 j_2 j_3 m_3 \right\rangle \left\langle \Phi \,\|\, O \,\|\, \Psi \right\rangle \tag{69}$$

$\left\langle j_1 j_2 m_1 m_2 \,|\, j_1 j_2 j_3 m_3 \right\rangle$ is the Clebsch–Gordan coefficient associated with the coupling of two angular momenta $\mathbf{J}_1$ and $\mathbf{J}_2$ to give $\mathbf{J}_3$,

$\left\langle \Phi \,\|\, O \,\|\, \Psi \right\rangle$ is the so-called **reduced matrix element**, that can depend on everything except the 3–components m_1, m_2 and m_3.

Using this result it is easy to see that the matrix elements of all vector operators for state vectors of definite angular momentum are parallel.

Indeed, let **A** and **B** be any pair of vectors. Applying the Wigner-Eckart theorem we have

$$\left\langle \Phi^{m_3}_{j_3} \left| A^{m_1}_1 \right| \Psi^{m_2}_{j_2} \right\rangle = \frac{1}{2j_3+1} \left\langle 1\, j_2\, m_1\, m_2 \,|\, 1\, j_2 j_3\, m_3 \right\rangle \left\langle \Phi \,\|\, \mathbf{A} \,\|\, \Psi \right\rangle . \tag{70}$$

$$\left\langle \Phi^{m_3}_{j_3} \left| B^{m_1}_1 \right| \Psi^{m_2}_{j_2} \right\rangle = \frac{1}{2j_3+1} \left\langle 1\, j_2\, m_1\, m_2 \,|\, 1\, j_2 j_3\, m_3 \right\rangle \left\langle \Phi \,\|\, \mathbf{B} \,\|\, \Psi \right\rangle . \tag{71}$$

Therefore, as long as $\langle \Phi \,\|\, \mathbf{B} \,\|\, \Psi \rangle$ does not vanish,

$$\left\langle \Phi^{m_3}_{j_3} \left| A^{m_1}_1 \right| \Psi^{m_2}_{j_2} \right\rangle = \frac{\langle \Phi \,\|\, \mathbf{A} \,\|\, \Psi \rangle}{\langle \Phi \,\|\, \mathbf{B} \,\|\, \Psi \rangle} \left\langle \Phi^{m_3}_{j_3} \left| B^{m_1}_1 \right| \Psi^{m_2}_{j_2} \right\rangle . \tag{72}$$

This is also true for the Cartesian components of the operators, A_i and B_i.

$$\left\langle \Phi^{m_3}_{j_3} \left| A_i \right| \Psi^{m_2}_{j_2} \right\rangle = \frac{\langle \Phi \,\|\, \mathbf{A} \,\|\, \Psi \rangle}{\langle \Phi \,\|\, \mathbf{B} \,\|\, \Psi \rangle} \left\langle \Phi^{m_3}_{j_3} \left| B_i \right| \Psi^{m_2}_{j_2} \right\rangle . \tag{73}$$

We could as well write the previous equation in vector notation, with the understanding that stands for three equations, one for each component

$$\left\langle \Phi_{j_3}^{m_3} \middle| \mathbf{A} \middle| \Psi_{j_2}^{m_2} \right\rangle = \frac{\langle \Phi \| \mathbf{A} \| \Psi \rangle}{\langle \Phi \| \mathbf{B} \| \Psi \rangle} \left\langle \Phi_{j_3}^{m_3} \middle| \mathbf{B} \middle| \Psi_{j_2}^{m_2} \right\rangle . \tag{74}$$

In particular, since $\mathbf{J}$ is itself a vector operator,

$$\left\langle \Phi_{j_2}^{m_3} \middle| \mathbf{A} \middle| \Psi_{j_2}^{m_2} \right\rangle = \frac{\langle \Phi \| \mathbf{A} \| \Psi \rangle}{\langle \Phi \| \mathbf{J} \| \Psi \rangle} \left\langle \Phi_{j_2}^{m_3} \middle| \mathbf{J} \middle| \Psi_{j_2}^{m_2} \right\rangle . \tag{75}$$

This last result has been written only for the case $j_2 = j_3$ because, since $\mathbf{J}$ commutes with $\mathbf{J}^2$, the reduced matrix element would vanish if Φ and Ψ had different angular momenta. However, m_2 and m_3 don't need to be equal because J_x and J_y do change the value of m_2.

Setting $j_2 = j$, $m_3 = m$, $m_2 = m'$ and the proportionality factor to C, the last equation can be written as

$$\left\langle \Phi_{j}^{m} \middle| \mathbf{A} \middle| \Psi_{j}^{m'} \right\rangle = C \left\langle \Phi_{j}^{m} \middle| \mathbf{J} \middle| \Psi_{j}^{m'} \right\rangle . \tag{76}$$

To evaluate the constant C we can do

$$\left\langle \Phi_j^m \left| \mathbf{A}\cdot\mathbf{J} \right| \Psi_j^m \right\rangle = \sum_{m'} \left\langle \Phi_j^m \left| \mathbf{A} \right| \Psi_j^{m'} \right\rangle \left\langle \Psi_j^{m'} \left| \mathbf{J} \right| \Psi_j^m \right\rangle, \tag{77}$$

and use the proportionality condition to write

$$\begin{aligned}\sum_{m'} \left\langle \Phi_j^m \left| \mathbf{A} \right| \Psi_j^{m'} \right\rangle \left\langle \Psi_j^{m'} \left| \mathbf{J} \right| \Psi_j^m \right\rangle &= C \sum_{m'} \left\langle \Phi_j^m \left| \mathbf{J} \right| \Psi_j^{m'} \right\rangle \left\langle \Psi_j^{m'} \left| \mathbf{J} \right| \Psi_j^m \right\rangle \\ &= C \left\langle \Phi_j^m \left| \mathbf{J}^2 \right| \Psi_j^m \right\rangle = C\, j(j+1)\hbar^2. \end{aligned} \tag{78}$$

Therefore

$$C = \frac{\left\langle \Phi_j^m \left| \mathbf{A}\cdot\mathbf{J} \right| \Psi_j^m \right\rangle}{j(j+1)\hbar^2}, \tag{79}$$

and

$$\boxed{\left\langle \Phi_j^m \left| \mathbf{A} \right| \Psi_j^{m'} \right\rangle = \frac{\left\langle \Phi_j^m \left| \mathbf{A}\cdot\mathbf{J} \right| \Psi_j^m \right\rangle}{j(j+1)\hbar^2} \left\langle \Phi_j^m \left| \mathbf{J} \right| \Psi_j^{m'} \right\rangle} \tag{80}$$

This special form of the Wigner–Eckart theorem is known as the **Landé formula**.

Time-independent perturbation theory.

Consider an unperturbed Hamiltonian, $\mathcal{H}_0$, with a set of orthonormal state vectors, ϕ_a, and corresponding eigenvalues E_a,

$$\mathcal{H}_0\phi_a = E_a\phi_a, \qquad \langle\phi_a\,|\,\phi_a\rangle = \delta_{ab}. \tag{81}$$

Now we add a small term $\delta\mathcal{H}$ to the Hamiltonian, proportional to some small parameter ε.

$$\mathcal{H} = \mathcal{H}_0 + \delta\mathcal{H}. \tag{82}$$

The energy values will then change to $E_a + \delta E_a$, with corresponding state vectors $\phi_a + \delta_a\phi_a$, where δE_a and $\delta\phi_a$ are presumably given by power series in ε,

$$\delta E_a = \delta_1 E_a + \delta_2 E_a + \ldots, \qquad \delta\phi_a = \delta_1\phi_a + \delta_2\phi_a + \ldots, \tag{83}$$

with $\delta_n E_a$ and $\delta_n\phi_a$ proportional to ε^n.

We will collect here the formulae needed to compute $\delta_1 E_a$, $\delta_2 E_a$, and $\delta_1\phi_a$.

First-order, non-degenerate case.

To first order, the shift in the energy of a bound state is the expectation value of the perturbation $\delta\mathcal{H}$ in the unperturbed state,

$$\boxed{\delta_1 E_a = \langle \phi_a \,|\, \delta\mathcal{H} \,|\, \phi_a \rangle} \tag{84}$$

For non-degenerate spectra ($E_a \neq E_b$ if $\phi_a \neq \phi_b$), the first order perturbation to ϕ_a is

$$\boxed{\delta_1 \phi_a = \sum_{b \neq a} \frac{\langle \phi_b \,|\, \delta\mathcal{H} \,|\, \phi_a \rangle}{(E_a - E_b)} \; |\phi_b\rangle} \tag{85}$$

First-order, degenerate case.

Suppose there are a number of states $\phi_{a_1}, \phi_{a_2}, \ldots, \phi_{a_n}$ with the same energy E_a.

In this case we perform a linear combination of the degenerate states ϕ_{a_r} to find a new set of sates ψ_{a_r} (also degenerate) for which the perturbation $\delta\mathcal{H}$ **is diagonal** (the off-diagonal matrix elements all vanish).

$$\psi_{a_m} = \sum_r u_{mr}\, \phi_{a_r}, \tag{86}$$

In terms of the new ψ states, the first-order energy shift and the first-order correction to the unperturbed state are given by

$$\boxed{\delta_1 E_a = \langle \psi_a \,|\, \delta\mathcal{H} \,|\, \psi_a \rangle} \tag{87}$$

$$\boxed{\delta_1 \psi_a = \sum_{b \neq a} \frac{\langle \psi_b \,|\, \delta\mathcal{H} \,|\, \psi_a \rangle}{(E_a - E_b)}\, |\psi_b\rangle} \tag{88}$$

If we are faced with a set of degenerate unperturbed states ϕ_{a_r} for which the matrix $\langle \phi_{a_s} | \delta\mathcal{H} | \phi_{a_r} \rangle$ is not diagonal, all we have to do is make it diagonal by finding its eigenvalues and eigenstates, ψ_{a_r}.

If we can find an observable $\mathcal{A}$ which commutes with both the unperturbed Hamiltonian $\mathcal{H}_0$ and the perturbation $\delta\mathcal{H}$, then it is easy to show that the perturbation has already a diagonal form if we work with simultaneous eigenstates of $\mathcal{H}_0$ and $\mathcal{A}$.

Indeed, let ψ_{a_1} and ψ_{a_2} be degenerate eigenstates of $\mathcal{H}_0$ which are also eigenstates of $\mathcal{A}$ with *different* eigenvalues,

$$\mathcal{A} |\psi_{a_1}\rangle = A_{a_1} |\psi_{a_1}\rangle , \qquad \mathcal{A} |\psi_{a_2}\rangle = A_{a_2} |\psi_{a_2}\rangle , \qquad \text{with } A_{a_1} \neq A_{a_2} .$$

Since by assumption $[\mathcal{A}, \delta\mathcal{H}] = 0$, and $\mathcal{A}$ is Hermitian, we have

$$\begin{aligned} 0 = \langle \psi_{a_1} | [\mathcal{A}, \delta\mathcal{H}] | \psi_{a_2} \rangle &= \langle \psi_{a_1} | \mathcal{A}\delta\mathcal{H} | \psi_{a_2} \rangle - \langle \psi_{a_1} | \delta\mathcal{H}\mathcal{A} | \psi_{a_2} \rangle \\ &= A_{a_1} \langle \psi_{a_1} | \delta\mathcal{H} | \psi_{a_2} \rangle - A_{a_2} \langle \psi_{a_1} | \delta\mathcal{H} | \psi_{a_2} \rangle = (A_{a_1} - A_{a_2}) \langle \psi_{a_1} | \delta\mathcal{H} | \psi_{a_2} \rangle . \end{aligned}$$

Therefore $\langle \psi_{a_1} | \delta\mathcal{H} | \psi_{a_2} \rangle = 0$ for $\psi_{a_1} \neq \psi_{a_2}$.

Second-order, non-degenerate case.

Besides $\delta_1\mathcal{H}$, we also include now in the Hamiltonian a possible term $\delta_2\mathcal{H}$ which is itself of second order in ε,

$$\mathcal{H} = \mathcal{H}_0 + \delta_1\mathcal{H} + \delta_2\mathcal{H}. \tag{89}$$

The second-order energy shift is given by

$$\boxed{\delta_2 E_a = \sum_{b\neq a} \frac{|\langle\phi_b|\,\delta_1\mathcal{H}\,|\phi_a\rangle|^2}{(E_a - E_b)} + \langle\phi_a|\,\delta_2\mathcal{H}\,|\phi_a\rangle} \tag{90}$$

When one says that an energy shift is produced by the emission and reabsorption of some virtual particle, as for instance the Lamb shift is produced by the emission and reabsorption of a virtual photon by the electron in the hydrogen atom, what is meant is that $\delta_2 E_a$ (or a higher-order correction) receives an important contribution from a state ϕ_b containing that particle.

Note that, if ϕ_a is the state of lowest energy of the system, then (in the absence of $\delta_2\mathcal{H}$) the second-order energy shift of its energy is always negative, because all other states have $E_b > E_a$.

Second-order, degenerate case.

In the degenerate case some of the states which we are interested in have the same unperturbed energies.

The second-order energy shift in this case is

$$\delta_2 E_a = \sum_{c:\, E_c \neq E_a} \frac{|\langle \phi_a | \delta_1 \mathcal{H} | \phi_c \rangle|^2}{(E_a - E_c)} + \langle \phi_a | \delta_2 \mathcal{H} | \phi_a \rangle \tag{91}$$

This is the same result as in the non-degenerate case (90), except that here we have to specify not only that the intermediate states ϕ_c have $c \neq a$, but also that they have $E_c \neq E_a$.

The Dirac equation.

By applying the standard quantum prescriptions

$$\mathbf{p} \to -i\hbar\boldsymbol{\nabla}, \qquad E \to i\hbar\frac{\partial}{\partial t}, \tag{92}$$

to the classical energy–momentum relation $\dfrac{\mathbf{p}^2}{2m} + V = E$, you get the Schrödinger equation,

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi = i\hbar\frac{\partial\Psi}{\partial t}. \tag{93}$$

It is easier to introduce the Dirac equation using relativistic four–vector notation. The energy-momentum *contravariant* four-vector, or four-momentum, is

$$p^\mu = (E/c, p_x, p_y, p_z) = (E/c, \mathbf{p}) = (p_0, p_1, p_2, p_3).$$

The corresponding *covariant* four-vector is is $p_\mu = (E/c, -\mathbf{p})$. You go from one to the other using *metric* tensor

$$\underbrace{g^{\mu\nu} = g_{\mu\nu}}_{\mathbf{g}} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}, \qquad p_\nu = g_{\mu\nu}p^\mu. \tag{94}$$

The scalar product of the four-momentum with itself is

$$p \cdot p = p^\mu g_{\mu\nu} p^\nu = p^\mu p_\mu = p_\mu p^\mu = p_0 p^0 + p_1 p^1 + p_2 p^2 + p_3 p^3$$
$$= p_0 p_0 - p_1 p_1 - p_2 p_2 - p_3 p_3 = \frac{E^2}{c^2} - p_x^2 - p_y^2 - p_z^2 = m^2 c^2.$$

The *same* quantum prescription holds in the relativistic regime

$$p_\mu = (E/c, -\mathbf{p}) \to i\hbar\partial_\mu, \qquad p^\mu = (E/c, \mathbf{p}) \to i\hbar\partial^\mu. \tag{95}$$

$$\partial_\mu \equiv \frac{\partial}{\partial x^\mu} = \left(\frac{1}{c}\frac{\partial}{\partial t}, \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right), \qquad \partial^\mu \equiv \frac{\partial}{\partial x_\mu} = \left(\frac{1}{c}\frac{\partial}{\partial t}, -\frac{\partial}{\partial x}, -\frac{\partial}{\partial y}, -\frac{\partial}{\partial z}\right).$$

$$\Box \equiv \partial^\mu \partial_\mu = \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} - \frac{\partial^2}{\partial z^2} = \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2 \tag{96}$$

The relation $E^2 - \mathbf{p}^2 c^2 = m^2 c^4$ can be written in covariant form as $c^2 p^\mu p_\mu = m^2 c^4$. The free-particle **Klein-Gordon** equation follows upon using in the equation $p^\mu p_\mu - m^2 c^2 = 0$, the canonical quantum prescription,

$$-\hbar^2 \partial^\mu \partial_\mu \Psi - m^2 c^2 \Psi = 0 \qquad -\frac{1}{c^2}\frac{\partial^2 \Psi}{\partial t^2} + \nabla^2 \Psi = \left(\frac{mc}{\hbar}\right)^2 \Psi. \tag{97}$$

A second-order equation in t was considered problematic at that time. Dirac searched for a first-order equation in t, compatible with the relation

$$p^\mu p_\mu - m^2c^2 = 0.$$

Suppose you are able to write

$$(p^\mu p_\mu - m^2c^2) = (\beta^\kappa p_\kappa + mc)(\gamma^\lambda p_\lambda - mc) = 0, \tag{98}$$

where a summation over repeated indices is understood and β^κ and γ^λ are eight coefficients to be determined.

Multiplying out the right hand side we have

$$p^\mu p_\mu - m^2c^2 = \beta^\kappa\gamma^\lambda p_\kappa p_\lambda - mc(\beta^\kappa - \gamma^\kappa)p_\kappa - m^2c^2. \tag{99}$$

For this equation to hold it is necessary that the linear term in p_κ disappear from the right hand side, therefore we must impose the condition $\beta^\kappa = \gamma^\kappa$.

We are left with

$$p^\mu p_\mu = \gamma^\kappa\gamma^\lambda p_\kappa p_\lambda. \tag{100}$$

The γ^κ coefficients cannot be just numbers. They should be matrices of, at least, dimension 4×4 and should satisfy the relation $\{\gamma^\mu, \gamma^\nu\} = \gamma^\mu\gamma^\nu + \gamma^\nu\gamma^\mu = 2g^{\mu\nu}$, where $g^{\mu\nu}$ is the metric tensor defined previously. We have then

$$(p^\mu p_\mu - m^2c^2) = (\gamma^\kappa p_\kappa + mc)(\gamma^\lambda p_\lambda - mc) = 0. \tag{101}$$

The **Dirac equation** is conventionally chosen to arise from the relation $(\gamma^\lambda p_\lambda - mc) = 0$,

$$(i\hbar\gamma^\mu\partial_\mu - mc)\Psi = 0 \tag{102}$$

We need an explicit representation of the γ matrices. The following is the most common convention adopted,

$$\gamma^0 = \begin{pmatrix} \mathbb{I} & 0 \\ 0 & -\mathbb{I} \end{pmatrix}, \quad \gamma^i = \begin{pmatrix} 0 & \sigma^i \\ -\sigma^i & 0 \end{pmatrix}, \quad i = 1, 2, 3 \tag{103}$$

where the Pauli matrices are given by

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{104}$$

$$\gamma^0 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}, \qquad \gamma^1 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix}, \tag{105}$$

$$\gamma^2 = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & i & 0 & 0 \\ -i & 0 & 0 & 0 \end{pmatrix}, \qquad \gamma^3 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}. \tag{106}$$

The following relations are useful,

$$[\sigma_i, \sigma_j] = 2i\sigma_k, \qquad \sigma_i\sigma_j = i\sigma_k, \qquad \sigma_i^2 = 1, \qquad \sigma_i\sigma_j + \sigma_j\sigma_i = 2\delta_{ij}, \tag{107}$$

$$\sigma_2\sigma_k^* = -\sigma_k\sigma_2, \qquad \sigma_i^\dagger = \sigma_i = \sigma_i^{-1}, \qquad \boldsymbol{\sigma} = (\sigma_1, \sigma_2, \sigma_3) \tag{108}$$

$$(\mathbf{a}\cdot\boldsymbol{\sigma})\cdot(\mathbf{b}\cdot\boldsymbol{\sigma}) = \mathbf{a}\cdot\mathbf{b} + i\boldsymbol{\sigma}\cdot(\mathbf{a}\times\mathbf{b}). \tag{109}$$

In the relation $\sigma_i\sigma_j = i\sigma_k$ the indices are understood to be an even permutation of $(1, 2, 3)$. A more general expression showing explicitly the Levi-Civita tensor is

$$\sigma_i\sigma_j = \delta_{ij} + i\epsilon_{ijk}\sigma_k.$$

The Dirac equation, $(i\hbar\gamma^\mu\partial_\mu - mc)\Psi = 0$, is written in a manifestly covariant form, but for our purposes it will be more convenient to write it using the following matrices

$$\beta \equiv \gamma^0, \quad \beta\alpha_1 = \gamma^1, \quad \beta\alpha_2 = \gamma^2, \quad \beta\alpha_3 = \gamma^3, \quad \alpha_k = \gamma^0\gamma^k. \tag{110}$$

Explicitly,

$$\beta = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}, \qquad \alpha_1 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}, \tag{111}$$

$$\alpha_2 = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix}, \qquad \alpha_3 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}. \tag{112}$$

And the equation, $i\hbar\left(\gamma^0\partial_0+\gamma^1\partial_1+\gamma^2\partial_2+\gamma^3\partial_3-\dfrac{mc}{i\hbar}\right)\Psi=0$, becomes

$$i\hbar\left(\beta\partial_0+\beta\alpha_1\partial_1+\beta\alpha_2\partial_2+\beta\alpha_3\partial_3-\frac{mc}{i\hbar}\right)\Psi=0. \tag{113}$$

Multiplying on the left by β we have (since $\beta^2=(\gamma^0)^2=1$)

$$i\hbar\left(\partial_0+\alpha_1\partial_1+\alpha_2\partial_2+\alpha_3\partial_3-\beta\frac{mc}{i\hbar}\right)\Psi=0, \tag{114}$$

$$i\hbar\partial_0\Psi=i\hbar\left(-\alpha_1\partial_1-\alpha_2\partial_2-\alpha_3\partial_3+\beta\frac{mc}{i\hbar}\right)\Psi. \tag{115}$$

But $i\hbar\left(-\alpha_1\partial_1-\alpha_2\partial_2-\alpha_3\partial_3\right)=\boldsymbol{\alpha}\mathbf{p}$ and $\partial_0=\frac{1}{c}\partial_t$, therefore

$$\frac{i\hbar}{c}\partial_t\Psi=\left(\boldsymbol{\alpha}\mathbf{p}+\beta mc\right)\Psi. \tag{116}$$

The operator $H_{\mathrm{D}}=c\boldsymbol{\alpha}\mathbf{p}+\beta mc^2$ is known as the Dirac Hamiltonian for a free particle. The time–independent Dirac equation for a free particle is

$$\boxed{(c\boldsymbol{\alpha}\mathbf{p}+\beta mc^2)\Psi=E\Psi} \tag{117}$$

Ψ is a four–component (bispinor) function,

$$\Psi = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix}. \tag{118}$$

In components, the free-particle Dirac equation, $(c\boldsymbol{\alpha}\mathbf{p} + \beta mc^2)\Psi = E\Psi$, becomes a set of four equations,

$$\begin{aligned} c(p_x - ip_y)\psi_4 + cp_z\psi_3 + (mc^2 - E)\psi_1 &= 0, \\ c(p_x + ip_y)\psi_3 - cp_z\psi_4 + (mc^2 - E)\psi_2 &= 0, \\ c(p_x - ip_y)\psi_2 + cp_z\psi_1 - (mc^2 + E)\psi_3 &= 0, \\ c(p_x + ip_y)\psi_1 - cp_z\psi_2 - (mc^2 + E)\psi_4 &= 0. \end{aligned} \tag{119}$$

Using the Pauli matrices we can write these equations in two–component form for the spinors ψ_u and ψ_v defined as

$$\psi_u = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}, \qquad \psi_v = \begin{pmatrix} \psi_3 \\ \psi_4 \end{pmatrix}. \tag{120}$$

$$c\boldsymbol{\sigma}\mathbf{p}\psi_v + (mc^2 - E)\psi_u = 0, \quad (121)$$
$$c\boldsymbol{\sigma}\mathbf{p}\psi_u - (mc^2 + E)\psi_v = 0. \quad (122)$$

From (121) we have $\psi_u = \dfrac{c\boldsymbol{\sigma}\mathbf{p}}{E - mc^2}\psi_v$.

To estimate the relative magnitude of ψ_u and ψ_v in the non-relativistic approximation, we use $(\mathbf{a}\cdot\boldsymbol{\sigma})\cdot(\mathbf{b}\cdot\boldsymbol{\sigma}) = \mathbf{a}\cdot\mathbf{b} + i\boldsymbol{\sigma}\cdot(\mathbf{a}\times\mathbf{b})$ to get $(\boldsymbol{\sigma}\mathbf{p})^2 = p^2$. Therefore $\boldsymbol{\sigma}\mathbf{p} = p \approx mv$.

$$E - mc^2 = \sqrt{(mc^2)^2 + p^2c^2} - mc^2 = mc^2\sqrt{1 + \left(\frac{p}{mc}\right)^2} - mc^2$$
$$= mc^2\left[1 + \frac{1}{2}\left(\frac{p}{mc}\right)^2 - \frac{1}{8}\left(\frac{p}{mc}\right)^4 + \ldots\right] - mc^2 = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \ldots \approx \frac{1}{2}mv^2$$

$$\frac{\psi_u}{\psi_v} = \frac{c\boldsymbol{\sigma}\mathbf{p}}{E - mc^2} \approx \frac{cmv}{\frac{1}{2}mv^2} = 2\frac{c}{v},$$

For $v/c \ll 1$ only the ψ_u component (also known as **large component**) needs to be considered.

Insert $\psi_v = \psi_u(E - mc^2)/(c\boldsymbol{\sigma}\mathbf{p})$ in $c\boldsymbol{\sigma}\mathbf{p}\psi_u - (mc^2 + E)\psi_v = 0$, to get

$$c\boldsymbol{\sigma}\mathbf{p}\psi_u - \frac{(mc^2 + E)(E - mc^2)}{c\boldsymbol{\sigma}\mathbf{p}}\psi_u = 0, \qquad c^2(\boldsymbol{\sigma}\mathbf{p})^2\psi_u = (E + mc^2)(E - mc^2)\psi_u \tag{123}$$

At non-relativistic energies we have $E' \equiv E - mc^2 \approx \frac{1}{2}mv^2 \ll mc^2$, so

$$(E - mc^2)(E + mc^2) = E'(E' + 2mc^2) = 2mc^2E'\left(1 + \frac{E'}{2mc^2}\right) \approx 2mc^2E'$$

Using this, and taking into account that $(\boldsymbol{\sigma}\mathbf{p})^2 = p^2$, equation (123) becomes

$$E'\psi_u = \frac{p^2}{2m}\psi_u, \qquad E'\psi_u = -\frac{\hbar^2}{2m}\nabla^2\psi_u. \tag{124}$$

This is still a two–component equation, but since both ψ_u components satisfy the relation, we may drop the subscript and write, generically

$$\boxed{E'\psi = -\frac{\hbar^2}{2m}\nabla^2\psi} \tag{125}$$

which is the time-independent Schrödinger equation for a free particle.

The electromagnetic coupling in the Dirac equation.

$$(i\hbar\gamma^\mu\partial_\mu - mc)\Psi = 0. \tag{126}$$

$$(i\hbar\gamma^\mu D_\mu - mc)\Psi = 0, \qquad D_\mu = \partial_\mu + i\frac{q}{c}A_\mu, \qquad A^\mu = (\phi, \mathbf{A}) \tag{127}$$

$$\mathbf{B} = \boldsymbol{\nabla}\times\mathbf{A}, \qquad \mathbf{E} = -\frac{1}{c}\frac{\partial\mathbf{A}}{\partial t} - \boldsymbol{\nabla}\phi. \tag{128}$$

$$H_0 = \boldsymbol{\alpha}c\mathbf{p} + \beta mc^2 \quad \longrightarrow \quad H = \boldsymbol{\alpha}\,(c\mathbf{p} - q\mathbf{A}) + \beta mc^2 + q\phi.$$

The Dirac equation for a particle in the presence of an electromagnetic field is

$$\Big[\boldsymbol{\alpha}(c\mathbf{p} - q\mathbf{A}) + \beta mc^2 + q\phi\Big]\psi = E\psi. \tag{129}$$

In two-component form

$$\boldsymbol{\sigma}(c\mathbf{p} - q\mathbf{A})\psi_v + (mc^2 + q\phi)\psi_u = E\psi_u, \tag{130}$$

$$\boldsymbol{\sigma}(c\mathbf{p} - q\mathbf{A})\psi_u - (mc^2 - q\phi)\psi_v = E\psi_v. \tag{131}$$

Let's examine more closely the *large* component. From the second equation,

$$\psi_v(E + mc^2 - q\phi) = \boldsymbol{\sigma}(c\mathbf{p} - q\mathbf{A})\psi_u, \qquad \psi_v = \frac{\boldsymbol{\sigma}(c\mathbf{p} - q\mathbf{A})}{E + mc^2 - q\phi}\psi_u. \tag{132}$$

Insert this in the first equation, denoting $E' = E - mc^2$ and $\boldsymbol{\pi} = \mathbf{p} - \frac{q}{c}\mathbf{A}$,

$$\boldsymbol{\sigma}(c\mathbf{p} - q\mathbf{A})\frac{\boldsymbol{\sigma}(c\mathbf{p} - q\mathbf{A})}{E + mc^2 - q\phi}\psi_u + (mc^2 + q\phi)\psi_u = E\psi_u, \tag{133}$$

$$(\boldsymbol{\sigma}\boldsymbol{\pi})\frac{c^2}{E' + 2mc^2 - q\phi}(\boldsymbol{\sigma}\boldsymbol{\pi})\,\psi_u = (E - mc^2 - q\phi)\psi_u = (E' - q\phi)\psi_u, \tag{134}$$

$$\frac{1}{2m}(\boldsymbol{\sigma}\boldsymbol{\pi})\frac{2mc^2}{E' + 2mc^2 - q\phi}(\boldsymbol{\sigma}\boldsymbol{\pi})\,\psi_u = (E' - q\phi)\psi_u, \tag{135}$$

$$(E' - q\phi)\psi_u = \frac{1}{2m}(\boldsymbol{\sigma}\boldsymbol{\pi})K(\boldsymbol{\sigma}\boldsymbol{\pi})\,\psi_u \tag{136}$$

$$K = \frac{2mc^2}{E' + 2mc^2 - q\phi} = \frac{1}{1 + \dfrac{E' - q\phi}{2mc^2}} = 1 - \frac{E' - q\phi}{2mc^2} + \ldots \tag{137}$$

$$\boxed{(E' - q\phi)\psi_u = \frac{1}{2m}(\boldsymbol{\sigma\pi})K(\boldsymbol{\sigma\pi})\,\psi_u} \tag{138}$$

Setting $K = 1$, $\qquad (E' - q\phi)\psi_u = \frac{1}{2m}(\boldsymbol{\sigma\pi})^2\,\psi_u,$

$$(\boldsymbol{\sigma\pi})^2 = (\boldsymbol{\pi})^2 + i\boldsymbol{\sigma}\cdot(\boldsymbol{\pi}\times\boldsymbol{\pi}).$$

$$(\boldsymbol{\sigma\pi})^2 = \left(\mathbf{p} - \frac{q}{c}\mathbf{A}\right)^2 - \frac{q\hbar}{c}\boldsymbol{\sigma}\cdot(\boldsymbol{\nabla}\times\mathbf{A})\,. \tag{139}$$

Under the approximation $K \approx 1$ we arrive then at the **Pauli equation**.

$$(E' - q\phi)\,\psi_u = \left[\frac{1}{2m}\left(\mathbf{p} - \frac{q}{c}\mathbf{A}\right)^2 - \frac{q\hbar}{2mc}\boldsymbol{\sigma}\cdot(\boldsymbol{\nabla}\times\mathbf{A})\right]\,\psi_u. \tag{140}$$

$$E'\,\psi_u = \left[\frac{1}{2m}\left(\mathbf{p} - \frac{q}{c}\mathbf{A}\right)^2 - \frac{q\hbar}{2mc}\boldsymbol{\sigma}\cdot(\boldsymbol{\nabla}\times\mathbf{A}) + q\phi\right]\,\psi_u. \tag{141}$$

It predicts an interaction term between the magnetic field, $\mathbf{B} = \boldsymbol{\nabla}\times\mathbf{A}$, and the spin operator of a spin 1/2 particle, $\mathbf{S} = \hbar\boldsymbol{\sigma}/2$.

The next higher approximation comes from doing[1]

$$K = \frac{1}{1 + \dfrac{E' - q\phi}{2mc^2}} \approx 1 - \frac{E' - q\phi}{2mc^2}. \tag{142}$$

Keeping only terms up to v^2/c^2,

$$\begin{aligned}(E' - q\phi)\,\psi \;=\; \Bigg[& \frac{1}{2m}\left(\mathbf{p} - \frac{q}{c}\mathbf{A}\right)^2 - \frac{q\hbar}{2mc}\boldsymbol{\sigma}\cdot(\boldsymbol{\nabla}\times\mathbf{A}) \\ & - \frac{p^4}{8m^3c^2} + \frac{\hbar^2 q}{8m^2c^2}\boldsymbol{\nabla}(\boldsymbol{\nabla}\phi) + \frac{\hbar q}{4m^2c^2}\boldsymbol{\sigma}\left[(\boldsymbol{\nabla}\phi)\times\mathbf{p}\right]\Bigg]\,\psi \end{aligned} \tag{143}$$

Set $q = -e$,

$$\begin{aligned}(E' + e\phi)\,\psi \;=\; \Bigg[& \frac{1}{2m}\left(\mathbf{p} + \frac{e}{c}\mathbf{A}\right)^2 + \frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot(\boldsymbol{\nabla}\times\mathbf{A}) \\ & - \frac{p^4}{8m^3c^2} - \frac{\hbar^2 e}{8m^2c^2}\boldsymbol{\nabla}^2\phi - \frac{\hbar e}{4m^2c^2}\boldsymbol{\sigma}\left[(\boldsymbol{\nabla}\phi)\times\mathbf{p}\right]\Bigg]\,\psi. \end{aligned} \tag{144}$$

[1] $1/(1+x) \approx 1 - x$ for small x.

In atomic spectroscopy it is common to work with inverse of centimeters as energy units. From the relation $1/\lambda = E/hc$, we have, for $E = 1\,\mathrm{eV}$.

$$\frac{1}{\lambda} = \frac{E}{2\pi\hbar c} = \frac{1}{2\pi \times 197.3269788(12) \times 10^{-7}}\ \mathrm{cm}^{-1} = 8065.544005\ \mathrm{cm}^{-1}. \quad (145)$$

- The scalar potential energy, $e\phi$, with a size of about $10^5\mathrm{cm}^{-1}$, or $\sim 12\mathrm{eV}$.
- The term $\frac{1}{2m}\left(\mathbf{p} + \frac{e}{c}\mathbf{A}\right)^2$ contains the kinetic energy and the interaction with the vector potential $\mathbf{A}$. It has also a size of about $10^5\mathrm{cm}^{-1}$ and is responsible of, or contributes to, several physical processes such as the absorption, emission and scattering of electromagnetic waves, diamagnetism and the Zeeman effect.
- The interaction of the electron spin magnetic moment with a magnetic field, $\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$, is given by $\frac{e\hbar}{2mc}\boldsymbol{\sigma} \cdot (\boldsymbol{\nabla} \times \mathbf{A})$, with an energy of about $1\mathrm{cm}^{-1}\ (1.2 \times 10^{-4}\mathrm{eV})$.

- The relativistic correction to the kinetic energy, $\frac{p^4}{8m^3c^2}$, with a size of about $0.1\mathrm{cm}^{-1}$ $(1.2\times10^{-5}\mathrm{eV})$, comes from the expansion of the relativistic kinetic energy

$$T=\frac{p^2}{2m}-\frac{p^4}{8m^3c^2}+\ldots$$

- The Darwin term, $\frac{\hbar^2e}{8m^2c^2}\boldsymbol{\nabla}^2\phi$, has no classic analogue and produces an energy shift in s–states by less than $0.1\mathrm{cm}^{-1}$.
- The spin-orbit interaction term is $-\frac{\hbar e}{4m^2c^2}\boldsymbol{\sigma}\left[(\boldsymbol{\nabla}\phi)\times\mathbf{p}\right]$, with a size from 10 to $10^3\,\mathrm{cm}^{-1}$, (0.0012 to 0.12 eV). If ϕ depends only on r the gradient is just $\boldsymbol{\nabla}\phi=\frac{d\phi}{dr}\frac{\mathbf{r}}{r}$.

  Using $\mathbf{L}=\mathbf{r}\times\mathbf{p}$ and $\mathbf{S}=\frac{\hbar}{2}\boldsymbol{\sigma}$, we obtain a more familiar expression

$$-\frac{\hbar e}{4m^2c^2}\boldsymbol{\sigma}\left[(\boldsymbol{\nabla}\phi)\times\mathbf{p}\right]=-\frac{e}{2m^2c^2}\frac{d\phi}{dr}\frac{1}{r}\mathbf{S}(\mathbf{r}\times\mathbf{p})=-\frac{e}{2m^2c^2}\frac{d\phi}{dr}\frac{1}{r}\mathbf{LS}\quad(146)$$

The hydrogen atom without higher-order corrections.

$$(E' + e\phi)\,\psi = \left[\frac{1}{2m}\left(\mathbf{p} + \frac{e}{c}\mathbf{A}\right)^2 + \frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot(\boldsymbol{\nabla}\times\mathbf{A}) - \frac{p^4}{8m^3c^2} - \frac{\hbar^2 e}{8m^2c^2}\boldsymbol{\nabla}^2\phi - \frac{\hbar e}{4m^2c^2}\boldsymbol{\sigma}\left[(\boldsymbol{\nabla}\phi)\times\mathbf{p}\right]\right]\psi. \quad (147)$$

$$(E' + e\phi)\,\psi = \frac{p^2}{2m}\,\psi. \quad (148)$$

$$(E' + e\phi)\,\psi \;=\; \frac{p^2}{2m}\,\psi. \tag{149}$$

At non-relativistic energies, $E' \approx mv^2/2$. Write E, instead of E', to simplify notation. Replace $\mathbf{p}$ by $-i\hbar\boldsymbol{\nabla}$ and write the electric scalar potential as $e\phi = -V$ to get

$$\boxed{\mathcal{H}\psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\,\psi \;=\; E\psi} \tag{150}$$

In spherical coordinates,

$$r^2\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)\psi + \frac{2mr^2}{\hbar^2}(E - V)\psi \;=\; L^2\psi, \tag{151}$$

where

$$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]. \tag{152}$$

Assume that the potential has only a radial dependence, $V = V(r)$, and that the eigenfunctions can be written as

$$\boxed{\psi(r,\theta,\varphi) = \frac{1}{r}u(r)Y(\theta,\varphi) = R(r)Y(\theta,\varphi)} \tag{153}$$

so the Schrödinger equation can be separated into

$$\frac{d^2u(r)}{dr^2} + \frac{2m}{\hbar^2}\big[E - V(r)\big]u(r) = \frac{\lambda}{r^2}u(r), \tag{154}$$

$$L^2Y(\theta,\varphi) = \lambda Y(\theta,\varphi), \tag{155}$$

where λ is a constant. Boundary conditions: ψ and its first derivatives must be everywhere continuous, single-valued and finite. The consequences of imposing these conditions are that

$$\lambda = \ell(\ell+1), \qquad (\ell = 0, 1, 2\ldots), \tag{156}$$

and that the functions $Y(\theta,\varphi)$ are the spherical harmonics, $Y_\ell^m(\theta,\varphi)$, with $m = -\ell, -\ell+1, \ldots, +\ell$. The equation for $u(r)$ reads now,

$$\left[\frac{d^2}{dr^2} + \frac{2m}{\hbar^2}[E - V(r)] - \frac{\ell(\ell+1)}{r^2}\right]u(r) = 0. \tag{157}$$

Solutions to this equation are searched for taking into account that $V(r) \to 0$ as $r \to \infty$. Asymptotically, as $r \to \infty$, the previous equation reduces to

$$\frac{d^2u(r)}{dr^2} + \frac{2m}{\hbar^2}Eu(r) = 0, \tag{158}$$

which has solutions of the form

$$u(r) = e^{\pm ar}, \qquad \text{with} \qquad a = \sqrt{-\frac{2m}{\hbar^2}E}. \tag{159}$$

For $E < 0$ the solution e^{+ar} *is not* acceptable, but e^{-ar} *is*. For $E > 0$ either sign in the exponent would satisfy the boundary conditions, but we will only consider bound states of the atom, that is, solutions with $E < 0$.

We should look for solutions of the form $u(r) = e^{-ar}f(r)$, where $f(r)$ is a function to be determined by the radial equation (157) and the boundary conditions.

Our problem is an electron of mass m interacting with a nucleus of charge Ze, so $V(r) = -Ze^2/r$ and the radial equation is

$$\boxed{\left[\frac{d^2}{dr^2} + \frac{2m}{\hbar^2}\left(E + \frac{Ze^2}{r}\right) - \frac{\ell(\ell+1)}{r^2}\right] u(r) = 0} \tag{160}$$

In Rydberg units, where the unit of length is taken to be the Bohr radius, a_0, and the unit of energy the magnitude of the ground state bounding energy of a Hydrogen with infinite nucleus mass, we have the relations.

$$r_R = \frac{r}{a_0}, \qquad E_R = \frac{E}{R_\infty}, \qquad \nabla_R^2 = a_0^2 \nabla^2, \qquad a_0 = \frac{\hbar^2}{me^2} = \frac{\hbar}{\alpha mc}, \tag{161}$$

$$R_\infty = \frac{1}{2}\left(\frac{e^2}{\hbar c}\right)^2 mc^2 = \frac{1}{2}\alpha^2 mc^2 = \frac{\hbar^2}{2ma_0^2}, \qquad \alpha = \frac{e^2}{\hbar c}, \tag{162}$$

Then

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}\right)\psi = E\psi \quad \longrightarrow \quad \left(-\nabla_R^2 - \frac{2Z}{r_R}\right)\psi = E_R\psi. \tag{163}$$

Also

$$\left[\frac{1}{a_0^2}\frac{d^2}{dr_R^2} + \frac{1}{a_0^2}E_R + \frac{1}{a_0^2}\frac{2Z}{r_R} - \frac{1}{a_0^2}\frac{\ell(\ell+1)}{r_R^2}\right] u(r_R) = 0. \tag{164}$$

Since in Rydberg units $a_0 = 1$ by definition, we get (writing r instead of r_R etc. from now on, to shorten the notation)

$$\boxed{\frac{d^2u(r)}{dr^2} + \left[E + \frac{2Z}{r} - \frac{\ell(\ell+1)}{r^2}\right] u(r) = 0} \tag{165}$$

Now we substitute $u(r) = e^{-ar} f(r)$ and get

$$\frac{d^2f}{dr^2} - 2a\frac{df}{dr} + \left[a^2 + E + \frac{2Z}{r} - \frac{\ell(\ell+1)}{r^2}\right] f = 0, \tag{166}$$

But $a^2 = -2mE/\hbar^2 = -2mE_R R_\infty/\hbar^2 = -E_R/a_0^2$, so when E is expressed in Rydberg units (where $a_0 = 1$) we have $a^2 = -E$ and the previous expression reduces to

$$\boxed{\frac{d^2f}{dr^2} - 2a\frac{df}{dr} + \left[\frac{2Z}{r} - \frac{\ell(\ell+1)}{r^2}\right] f = 0} \tag{167}$$

Next, we try a power series solution,

$$f = r^s \left(A_0 + A_1 r + A_2 r^2 + \ldots\right), \tag{168}$$

with $s > 0$ to ensure that f remains finite as $r \to 0$.

It is found that $s = \ell + 1 > 0$ and that the following recursion relation for the coefficients must hold,

$$\frac{A_k}{A_{k-1}} = 2\,\frac{(\ell+k)a - Z}{k^2 + (2\ell+1)k} = 2\,\frac{\frac{\ell a}{k} + a - \frac{Z}{k}}{k + 2\ell + 1} \quad \longrightarrow \quad \frac{2a}{k} \tag{169}$$

We see that, for $k \to \infty$, the recursion relation behaves as $\dfrac{A_k}{A_{k-1}} \to \dfrac{2a}{k}$. This is also what happens to the coefficients of the e^{2ar} power series expansion,

$$e^{2ar} = \sum_{k=0}^{\infty} \frac{(2a)^k}{k!} r^k, \qquad \frac{(2a)^k/k!}{(2a)^{k-1}/(k-1)!} = \frac{2a}{k}. \tag{170}$$

This means the function $f(r)$ behaves like e^{2ar} for large k and, therefore, $u(r) = e^{-ar} f(r) \approx e^{-ar} e^{2ar} = e^{ar}$ for large k if $f(r)$ is given by an infinite series expansion. Since this implies that $u(r) \to \infty$ for $r \to \infty$, the series (168) **must terminate** at some finite value of k. This can only be done by setting to zero the numerator of the recursion relation (169).

Recalling that $a^2 = -E$ **in Rydberg units**,

$$(\ell + k)a - Z = 0, \qquad a = \frac{Z}{\ell + k}, \qquad \boxed{E = -\frac{Z^2}{(\ell + k)^2} \equiv -\frac{Z^2}{n^2}} \tag{171}$$

In SI units,

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{Z^2}{n^2} = -\frac{1}{2}mc^2\left(\frac{e^2}{4\pi\epsilon_0\hbar c}\right)^2\frac{Z^2}{n^2} = -\frac{1}{2}\alpha^2 mc^2\frac{Z^2}{n^2} = \frac{E_1^2}{n^2}$$

The boundary conditions have forced the bound states to have a *discrete* energy spectrum.

The acceptable solutions for $u(r)$ can be written in terms of the Laguerre polynomials,

$$L_{n+\ell}^{2\ell+1}(x) = -\left[(n+\ell)!\right]^2 \sum_{k=0}^{n-\ell-1} \frac{(-x)^k}{k!(n-\ell-k-1)!(2\ell+k+1)!}$$
$$= B_0 + B_1 x + B_2 x^2 + \ldots + B_{n-\ell-1}x^{n-\ell-1}. \tag{172}$$

$$L_{n+\ell}^{2\ell+1}(x) = -\left[(n+\ell)!\right]^2 \sum_{k=0}^{n-\ell-1} \frac{(-x)^k}{k!(n-\ell-k-1)!(2\ell+k+1)!}$$
$$= B_0 + B_1 x + B_2 x^2 + \ldots + B_{n-\ell-1} x^{n-\ell-1}. \quad (173)$$

$$B_k = -B_{k-1}\frac{n-\ell-k}{k(2\ell+k+1)}, \qquad B_{n-\ell-1} = (-1)^{n-\ell}\frac{(n+\ell)!}{(n-\ell-1)!} \quad (174)$$

To keep the order of the Laguerre polynomial finite, the acceptable values for the integer n are those that make the relation $n-\ell-1$ to be equal to zero or to some positive integer, therefore

$$n = \ell+1, \ell+2, \ell+3, \ldots \quad (175)$$

The full solution for the Hydrogen bound states is,

$$|n\ell m\rangle \equiv \psi_{n\ell m}(r,\theta,\varphi) = R_{n\ell}(r)\,Y_\ell^m(\theta,\varphi) = \frac{1}{r}u_{n\ell}(r)\,Y_\ell^m(\theta,\varphi), \quad (176)$$

$$|n\ell m\rangle \equiv \psi_{n\ell m}(r,\theta,\varphi) = R_{n\ell}(r)\,Y_\ell^m(\theta,\varphi) = \frac{1}{r}u_{n\ell}(r)\,Y_\ell^m(\theta,\varphi), \tag{177}$$

where,

$$u_{n\ell}(r) = \sqrt{\frac{(n-\ell-1)!Z}{n^2[(n+\ell)!]^3 a_0}}\left(\frac{2Zr}{na_0}\right)^{\ell+1} e^{-Zr/(na_0)}\, L_{n+\ell}^{2\ell+1}\left(\frac{2Zr}{na_0}\right), \tag{178}$$

and

$$\int_0^\infty u_{n\ell}(r)u_{n'\ell}(r)\,dr = \delta_{nn'}. \tag{179}$$

The orthogonality properties of $u_{n\ell}(r)$ and $Y_\ell^m(\theta,\varphi)$ lead to the following orthogonality relations for the Hydrogen eigenfunctions.

$$\langle n\ell m|n'\ell' m'\rangle = \int \psi^*_{n\ell m}(r,\theta,\varphi)\psi_{n'\ell' m'}(r,\theta,\varphi)\,d\tau = \delta_{nn'}\delta_{\ell\ell'}\delta_{mm'}. \tag{180}$$

Three quantum numbers: n, ℓ, m, taking the values

$$n = 1, 2, 3, \ldots, \qquad \ell = 0, 1, 2, \ldots (n-1)$$

$$m = -\ell, \ell+1, \ldots, 0, \ldots \ell-1, +\ell$$

Spectroscopic notation, $s, p, d, f, g \ldots$ for $\ell = 0, 1, 2, 3, 4, \ldots$.

The degeneracy of the Hydrogen eigenstates is $\sum_{\ell=0}^{n-1}(2\ell+1) = n^2$.

Hydrogenic wave functions for the states with $n = 1$ and $n = 2$

$$\psi_{100}(r,\theta,\varphi) = \left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{\sqrt{\pi}}\, e^{-Zr/a_0}, \qquad \psi_{100}(r=0) \neq 0$$

$$\psi_{200}(r,\theta,\varphi) = \left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{\sqrt{32\pi}} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}, \qquad \psi_{200}(r=0) \neq 0$$

$$\psi_{210}(r,\theta,\varphi) = \left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{\sqrt{32\pi}} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos\theta, \qquad \psi_{210}(r=0) = 0$$

$$\psi_{21\pm1}(r,\theta,\varphi) = \left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{\sqrt{32\pi}} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin\theta\, e^{\pm i\varphi}, \qquad \psi_{21\pm1}(r=0) = 0$$

For a given ℓ, the number of nodes in $R_{n\ell}(r)$ increases with n.

The probability of finding an electron in an element of volume $d\tau$ is

$$\psi^*\psi\, d\tau = \frac{1}{r^2} u_{n\ell}^2(r)\, Y_\ell^{m*}(\theta,\varphi)\, Y_\ell^m(\theta,\varphi)\, r^2 \sin\theta\, dr\, d\theta\, d\varphi. \tag{181}$$

$u_{n\ell}^2(r)\,\mathrm{d}r$ is a radial charge density in the same sense that $\psi^*\psi$ is a charge density.

The probability of finding the electron between θ and $\theta + d\theta$ is proportional to

$$Y_\ell^{m*}(\theta,\varphi)\, Y_\ell^m(\theta,\varphi) \sin\theta d\theta = \left[P_\ell^{|m|}(\cos\theta)\right]^2 \sin\theta d\theta. \tag{182}$$

The prob. of finding the electron between φ and $\varphi + d\varphi$ is proportional to $d\varphi$.

The bound states form an infinite discrete set, but it is not complete.

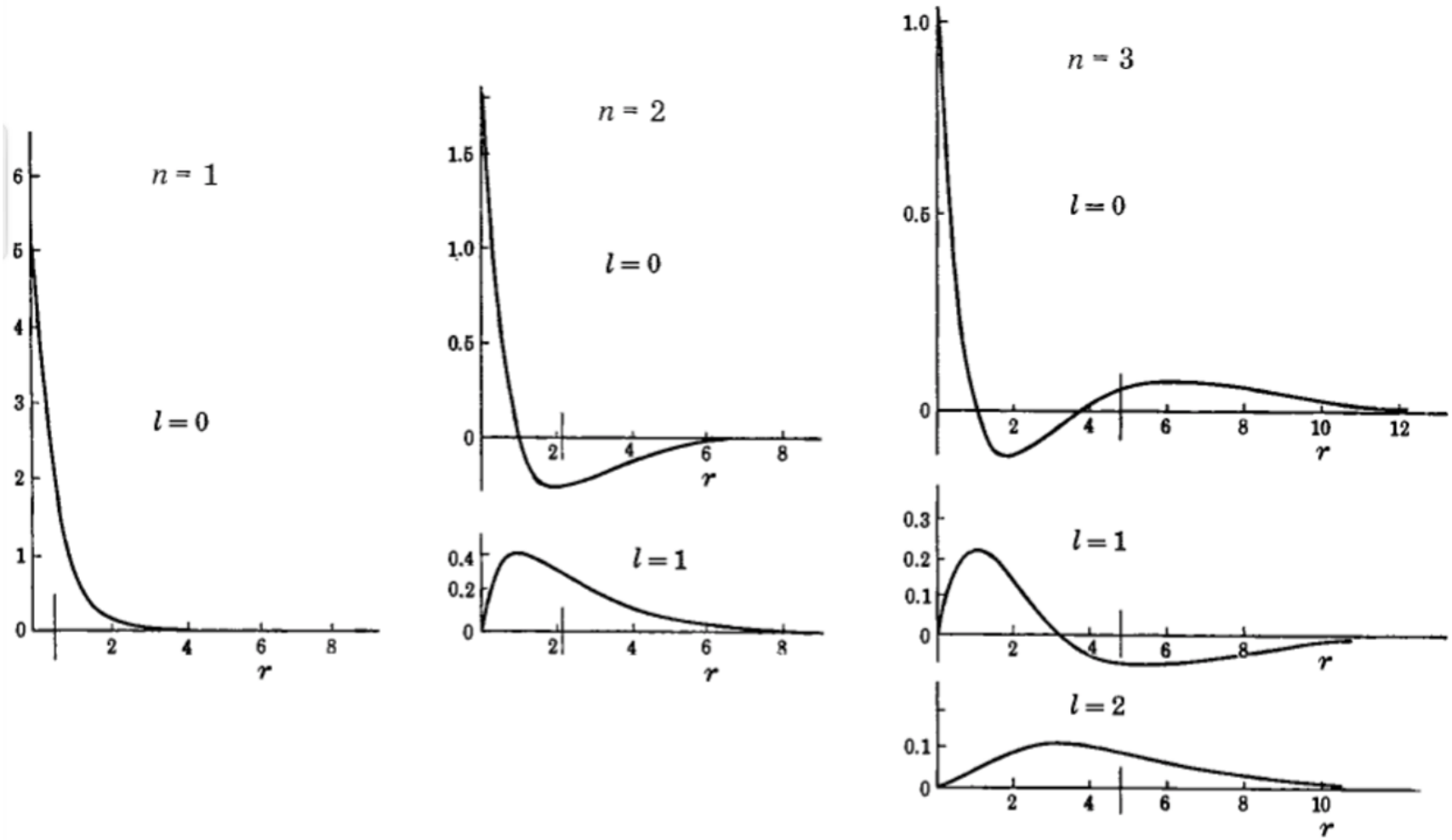
$\mathbf{L} = \mathbf{r} \times \mathbf{p}$, commutes with ∇^2, so the Hamiltonian $\mathcal{H} = -(\hbar^2/2m)\nabla^2 + V(r)$ also commutes with $\mathbf{L}$ and L^2.

$$[L^2, \mathcal{H}] = [L_z, \mathcal{H}] = 0. \tag{183}$$

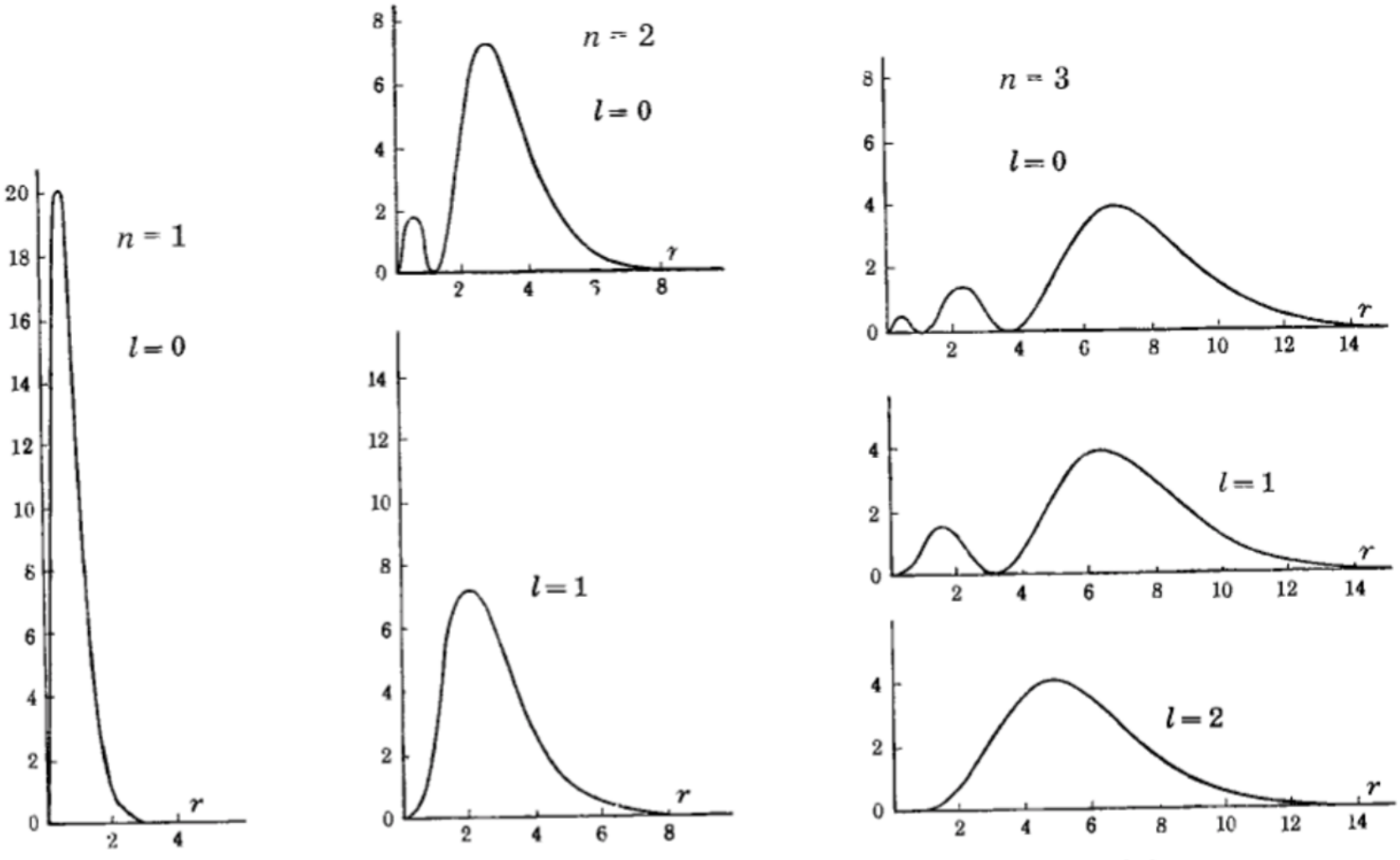
Since this Hamiltonian does not contain spin operators, the following relations also hold,

$$[S^2, \mathcal{H}] = [S_z, \mathcal{H}] = 0. \tag{184}$$

The radial part, $R_{nl}(r) = \frac{1}{r}u_{nl}(r)$, of the Hydrogen wave function.



Radial charge density part $[u_{nl}(r)]^2$ of the Hydrogen wave function.



Expectation values.

$$\langle r^k \rangle = \int r^k \psi^* \psi \, d\tau = \int_0^\infty r^k R_{n\ell}^2(r) \, r^2 \, dr = \int_0^\infty r^k u_{n\ell}^2(r) \, dr. \tag{185}$$

$$\langle r \rangle_{n\ell} = \frac{a_0}{2Z} \left[3n^2 - \ell(\ell+1) \right]. \tag{186}$$

This may be interpreted as the *size* of the atom. Inversely proportional to Z.

For $\ell = 0$, the value of $\langle r \rangle_{n\ell}$ is proportional to n^2, the deviations from this proportionality being small for $\ell \neq 0$.

For Hydrogen, $\langle r \rangle = 3a_0/2$, while the maximum value of the probability density function (pdf) occurs at value of r given by $r_{\max} = a_0$.

For $\ell = n - 1$ the pdf has a single maximum at $r_{\max} = a_0 n^2/Z$.

$$\langle r^2 \rangle_{n\ell} = \frac{a_0^2}{Z^2} \frac{n^2}{2} \left[5n^2 + 1 - 3\ell(\ell+1) \right]. \tag{187}$$

We will need at some point to use the expectation value of several inverse powers of r.

$$\left\langle \frac{1}{r} \right\rangle_{n\ell} = \int_0^\infty \frac{1}{r} u_{n\ell}^2(r)\, dr = \frac{Z}{a_0}\frac{1}{n^2}, \qquad \left\langle \frac{1}{r^2} \right\rangle_{n\ell} = \frac{Z^2}{a_0^2}\frac{1}{n^3(\ell+\frac{1}{2})}. \tag{188}$$

$$\left\langle \frac{1}{r^3} \right\rangle_{n\ell} = \frac{Z^3}{a_0^3}\frac{1}{n^3(\ell+1)(\ell+\frac{1}{2})\ell}. \tag{189}$$

$$\left\langle \frac{1}{r^4} \right\rangle_{n\ell} = \frac{Z^4}{a_0^4}\frac{3n^2-\ell(\ell+1)}{2n^5(\ell+\frac{3}{2})(\ell+1)(\ell+\frac{1}{2})\ell(\ell-\frac{1}{2})}. \tag{190}$$

One-electron wave functions.

The Hamiltonian of the free–particle Schrödinger equation, $\mathcal{H} = p^2/2m$, commutes with the orbital angular momentum, $\mathbf{L}$, but the Hamiltonian of the free–particle Dirac equation does not:

$$[\mathcal{H}_{\rm D}, \mathbf{L}] \neq 0, \qquad \mathcal{H}_{\rm D} = c\boldsymbol{\alpha}\mathbf{p} + \beta mc^2, \tag{191}$$

where $\beta = \gamma^0$ and $\alpha_k = \gamma^0\gamma^k$, $(k = 1, 2, 3)$. It does commute, however, with the total angular momentum operator $\mathbf{J} = \mathbf{L} + \mathbf{S}$, where the spin operator is defined as

$$\mathbf{S} = \frac{\hbar}{2}\begin{pmatrix} \boldsymbol{\sigma} & 0 \\ 0 & \boldsymbol{\sigma} \end{pmatrix} \equiv \frac{\hbar}{2}\boldsymbol{\Sigma}, \qquad S_i = \frac{\hbar}{2}\begin{pmatrix} \sigma_i & 0 \\ 0 & \sigma_i \end{pmatrix}, \quad i = 1, 2, 3 \tag{192}$$

$$\mathbf{S}^2 = \frac{\hbar^2}{4}\begin{pmatrix} \sigma_1^2 & 0 \\ 0 & \sigma_1^2 \end{pmatrix} + \frac{\hbar^2}{4}\begin{pmatrix} \sigma_2^2 & 0 \\ 0 & \sigma_2^2 \end{pmatrix} + \frac{\hbar^2}{4}\begin{pmatrix} \sigma_3^2 & 0 \\ 0 & \sigma_3^2 \end{pmatrix} \tag{193}$$

$$\mathbf{S}^2 = \frac{3\hbar^2}{4}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \tag{194}$$

The components of $\mathbf{S}$ satisfy $[S_i, S_j] = i\hbar S_k$, with (i, j, k) an even permutation of $(1, 2, 3)$.

A particle at rest ($\mathbf{L} = 0$) satisfying the Dirac equation is described by a spinor which verifies the eigenvalue equation

$$\mathbf{S}^2\chi = \hbar^2 S(S+1)\chi = \hbar^2 \frac{3}{4}\chi,$$

This means that has an intrinsic angular momentum (spin) of $S = 1/2$.

The ability to **"automatically" incorporate** in such a way **the spin** of the electron was historically one of the great accomplishments of the Dirac equation.

The notation $\phi(\boldsymbol{r}) \equiv \phi_{n\ell m_\ell}(r, \theta, \varphi)$ stands for a one-electron **spatial orbital** with quantum numbers n, ℓ and m_ℓ.

The one-electron **spin functions** are

$$\chi_{m_s} \equiv \chi(m_s) = \begin{cases} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = |\tfrac{1}{2}, +\tfrac{1}{2}\rangle\,, & \text{for } m_s = +\tfrac{1}{2} \\ \begin{pmatrix} 0 \\ 1 \end{pmatrix} = |\tfrac{1}{2}, -\tfrac{1}{2}\rangle\,, & \text{for } m_s = -\tfrac{1}{2} \end{cases} \tag{195}$$

The full one-electron orbital is

$$\psi(\lambda) = \psi(r, \theta, \varphi, m_s) = \phi(\boldsymbol{r})\chi(m_s). \tag{196}$$

Dirac notation: $|\ell s m_\ell m_s\rangle$ stands for the angular and spin parts of the wave function.

The spin orbitals $\psi(\lambda) = |n\ell s m_\ell m_s\rangle$ are eigenfunctions of $\mathcal{H} = \dfrac{p^2}{2m} - \dfrac{Ze^2}{r}$, with the same energy eigenvalues associated to $\phi_{n\ell m_\ell}(r, \theta, \varphi)$. However, the degeneracy has been increased from n^2 to $2n^2$.

$$\begin{aligned}
L^2 |\ell s m_\ell m_s\rangle &= \ell(\ell+1)\hbar^2 |\ell s m_\ell m_s\rangle , \\
S^2 |\ell s m_\ell m_s\rangle &= s(s+1)\hbar^2 |\ell s m_\ell m_s\rangle = \frac{3}{4}\hbar^2 |\ell s m_\ell m_s\rangle , \\
L_z |\ell s m_\ell m_s\rangle &= m_\ell \hbar |\ell s m_\ell m_s\rangle , \\
S_z |\ell s m_\ell m_s\rangle &= m_s \hbar |\ell s m_\ell m_s\rangle = \pm\frac{1}{2}\hbar |\ell s m_\ell m_s\rangle .
\end{aligned} \tag{197}$$

We are free to make any linear combination of degenerate eigenfunctions to build other sets of degenerate eigenfunctions. A specially important example is

$$|\ell s j m\rangle = \sum_{m_\ell m_s} |\ell s m_\ell m_s\rangle \langle \ell s m_\ell m_s | \ell s j m\rangle \,, \tag{198}$$

where $\langle \ell s m_\ell m_s | \ell s j m\rangle$ are the Clebsh-Gordan coefficients for the coupling of $\mathbf{L}$ and $\mathbf{S}$ to obtain the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$.

The $|\ell s j m\rangle$ eigenstates satisfy

$$\begin{aligned} L^2 |\ell s j m\rangle &= \ell(\ell+1)\hbar^2 |\ell s j m\rangle \,, \\ S^2 |\ell s j m\rangle &= s(s+1)\hbar^2 |\ell s j m\rangle = \frac{3}{4}\hbar^2 |\ell s j m\rangle \,, \\ J^2 |\ell s j m\rangle &= j(j+1)\hbar^2 |\ell s j m\rangle \,, \\ J_z |\ell s j m\rangle &= m\hbar |\ell s j m\rangle \,. \end{aligned} \tag{199}$$

And,

$$j = \ell - \frac{1}{2}, \quad \ell + \frac{1}{2}, \qquad\qquad m = m_\ell + m_s \tag{200}$$

The $|\ell s j m\rangle$ states are not eigenfunctions of L_z or S_z. They are said to be in the **coupled representation**, in contrast to the $|\ell s m_\ell m_s\rangle$ states, which are in the **uncoupled representation**.

In the spectroscopic notation for the orbitals, the small case letters s, p, d, f, ... stand for $\ell = 0, 1, 2, 3, \ldots$ in the $|\ell s m_\ell m_s\rangle$ representation.

In the coupled representation $|\ell s j m\rangle$ (also called terms) we use upper case letters, S, P, D, F, ... to stand for $\ell = 0, 1, 2, 3, \ldots$, and the spin s is indicated by writing $2s+1$ as a superscript to the left.

For example,

$$^{2s+1}\mathrm{L}_j \;=\; ^{2}\mathrm{D}_{3/2}$$

means $\ell = 2$, $2s+1 = 2$ or $s = 1/2$. The value of the total angular momentum, $j = 3/2$, is written as a subscript, and m may be indicated separately as follows

$$|\ell s j m\rangle = \left|2\frac{1}{2}\frac{3}{2} - \frac{1}{2}\right\rangle = \left|^{2}\mathrm{D}_{3/2} - \frac{1}{2}\right\rangle . \tag{201}$$

In the coupled representation the states cannot be written as a product of a single space-wavefunction and a spinor, because **the angular part** of the wavefunction **is different for the two components of the spinor**.

Let's find the explicit form of the one-electron wavefunctions which are simultaneously eigenstates of L^2, S^2, J^2 and J_z.

Since the total angular momentum is

$$\mathbf{J} = \mathbf{L} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{\hbar}{2}\boldsymbol{\sigma}, \tag{202}$$

The J_z operator can be written as

$$J_z = -i\hbar \begin{pmatrix} \frac{\partial}{\partial\varphi} & 0 \\ 0 & \frac{\partial}{\partial\varphi} \end{pmatrix} + \frac{\hbar}{2}\sigma_3 = \hbar \begin{pmatrix} -i\frac{\partial}{\partial\varphi} + \frac{1}{2} & 0 \\ 0 & -i\frac{\partial}{\partial\varphi} - \frac{1}{2} \end{pmatrix}. \tag{203}$$

From this expression, it is easy to see that the eigenfunction of J_z corresponding to the eigenvalue $m\hbar$ can be written as

$$\Psi = \begin{pmatrix} R_1(r)F_1(\theta)\, e^{i(m-\frac{1}{2})\varphi} \\ R_2(r)F_2(\theta)\, e^{i(m+\frac{1}{2})\varphi} \end{pmatrix}, \tag{204}$$

For Ψ to be an eigenfunction of L^2, we need to require that $L^2\Psi = \ell(\ell+1)\hbar^2\Psi$.

$$\begin{aligned} L^2 R_1(r)F_1(\theta)\, e^{i(m-\frac{1}{2})\varphi} &= \ell(\ell+1)\hbar^2 R_1(r)F_1(\theta)\, e^{i(m-\frac{1}{2})\varphi}, \\ L^2 R_2(r)F_2(\theta)\, e^{i(m+\frac{1}{2})\varphi} &= \ell(\ell+1)\hbar^2 R_2(r)F_2(\theta)\, e^{i(m+\frac{1}{2})\varphi}. \end{aligned} \tag{205}$$

Since we know that $L^2\, Y_\ell^m = \ell(\ell+1)\hbar^2\, Y_\ell^m$, we conclude

$$F_1(\theta)\, e^{i(m-\frac{1}{2})\varphi} = Y_\ell^{m-\frac{1}{2}}(\theta,\varphi), \qquad F_2(\theta)\, e^{i(m+\frac{1}{2})\varphi} = Y_\ell^{m+\frac{1}{2}}(\theta,\varphi),$$

Therefore

$$\Psi = \begin{pmatrix} R_1(r)\, Y_\ell^{m-\frac{1}{2}}(\theta,\varphi) \\ R_2(r)\, Y_\ell^{m+\frac{1}{2}}(\theta,\varphi) \end{pmatrix}. \tag{206}$$

Finally, we need to add the requirement that Ψ is an eigenfunction of $J^2 = L^2 + S^2 + 2\mathbf{LS}$.

$J^2 = L^2 + S^2 + 2\mathbf{LS}$. When acting on Ψ, the eigenvalues of L^2 and S^2 are $\ell(\ell+1)\hbar^2$ and $3\hbar^2/4$, respectively. Therefore we can write

$$J^2 = \ell(\ell+1)\hbar^2 + \frac{3}{4}\hbar^2 + \hbar\mathbf{L}\boldsymbol{\sigma} = \hbar^2 \begin{pmatrix} \ell(\ell+1) + \frac{3}{4} + \frac{1}{\hbar}L_z & \frac{1}{\hbar}L_- \\ \frac{1}{\hbar}L_+ & \ell(\ell+1) + \frac{3}{4} - \frac{1}{\hbar}L_z \end{pmatrix},$$

where

$$L_\pm Y_\ell^m = (L_x \pm iL_y) Y_\ell^m = \hbar\sqrt{\ell(\ell+1) - m(m\pm 1)}\, Y_\ell^m.$$

Imposing the condition $J^2\Psi = j(j+1)\hbar^2\,\Psi$, we get a system of two equations which can be solved to obtain the following normalized eigenfunctions

$$\Psi_{\ell,j=\ell+\frac{1}{2},m} = \frac{R_{j-\frac{1}{2}}(r)}{\sqrt{2\ell+1}} \begin{pmatrix} \sqrt{\ell+m+\frac{1}{2}}\, Y_\ell^{m-\frac{1}{2}} \\ \sqrt{\ell-m+\frac{1}{2}}\, Y_\ell^{m+\frac{1}{2}} \end{pmatrix}, \quad j = \ell + \frac{1}{2}, \quad \ell = 0, 1, 2, \ldots$$

$$\Psi_{\ell,j=\ell-\frac{1}{2},m} = \frac{R_{j+\frac{1}{2}}(r)}{\sqrt{2\ell+1}} \begin{pmatrix} \sqrt{\ell-m+\frac{1}{2}}\, Y_\ell^{m-\frac{1}{2}} \\ -\sqrt{\ell+m+\frac{1}{2}}\, Y_\ell^{m+\frac{1}{2}} \end{pmatrix}, \quad j = \ell - \frac{1}{2}, \quad \ell = 1, 2, 3, \ldots$$

The case $\ell = 0$ must be treated separately. If $\ell = 0$ we only have the spin part and the J_z operator becomes

$$J_z = \frac{\hbar}{2}\sigma_3 = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

The eigenfunctions of L^2, S^2, J^2 and J_z can then be written for $\ell = 0$ as

$$\Psi_{n,\ell=0,j=\frac{1}{2},m} = R_{n,0}(r)\, Y_0^0(\theta,\varphi) \begin{pmatrix} m+\frac{1}{2} \\ \frac{1}{2}-m \end{pmatrix}, \qquad j = \frac{1}{2}, \quad \ell = 0. \tag{207}$$

In this case there is no angular dependence inside the spinor and the state is written as a separate product of a space-wavefunction and a constant spinor. The states for the two possible values of the magnetic quantum number m are

$$\begin{aligned} \Psi_{n,\ell=0,j=\frac{1}{2},m=\frac{1}{2}} &= R_{n,0}(r)\, Y_0^0(\theta,\varphi) \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \\ \Psi_{n,\ell=0,j=\frac{1}{2},m=-\frac{1}{2}} &= R_{n,0}(r)\, Y_0^0(\theta,\varphi) \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \end{aligned} \tag{208}$$

Spin-orbit coupling.

If the electrostatic potential depends only on r, from equation (146) we read off the following spin-orbit Hamiltonian,

$$\mathcal{H}_{\rm so} = -\frac{e}{2m^2c^2}\frac{1}{r}\frac{d\phi}{dr}\mathbf{LS} = \xi(r)\mathbf{LS}. \tag{209}$$

For hydrogen-like atoms $\phi = Ze/r$, therefore

$$\xi(r) = \frac{Ze^2}{2m^2c^2r^3}. \tag{210}$$

The one-electron Hamiltonian with spin-orbit coupling becomes $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\rm so}$, where

$$\mathcal{H}_0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}, \qquad \mathcal{H}_{\rm so} = \xi(r)\mathbf{LS}. \tag{211}$$

The term $\mathcal{H}_{\rm so}$ will be treated as a small perturbation. If the hydrogenic states $|n\ell sjm\rangle$ were non-degenerate, the first-order correction to the energy obtained from time-independent perturbation theory would be

$$E_n^{(1)} = \left\langle \psi_n^{(0)} \middle| \mathcal{H}_{\rm so} \middle| \psi_n^{(0)} \right\rangle. \tag{212}$$

However, $\mathcal{H}_0$ has degenerate eigenvalues (there are a number of eigenstates $\psi_{ni}^{(0)}$ with the same eigenvalue), so the first-order corrections to the energy are obtained from the solutions of the secular equation,

$$\left| H_{ij}^{\rm so} - E_n^{(1)}\delta_{ij} \right| = 0, \qquad \text{where} \qquad H_{ij}^{\rm so} = \left\langle \psi_{ni}^{(0)} \right| \mathcal{H}_{\rm so} \left| \psi_{nj}^{(0)} \right\rangle , \tag{213}$$

and $\psi_{ni}^{(0)}, \psi_{nj}^{(0)}$ are degenerate eigenfunctions of $\mathcal{H}_0$.

To decide the basis to compute the matrix elements, note that

$$\mathbf{J} = \mathbf{L} + \mathbf{S}, \qquad J^2 = L^2 + S^2 + 2\mathbf{LS}, \qquad \mathbf{LS} = \frac{1}{2}(J^2 - L^2 - S^2), \tag{214}$$

$$\left[\mathcal{H}_0, L^2\right] = \left[\mathcal{H}_0, S^2\right] = \left[\mathcal{H}_0, J^2\right] = [\mathcal{H}_0, L_\mu] = [\mathcal{H}_0, S_\mu] = [\mathcal{H}_0, J_\mu] = 0, \tag{215}$$

where L_μ, S_μ and J_μ stand for any component (rectangular or spherical) of $\mathbf{L}$, $\mathbf{S}$ and $\mathbf{J}$, respectively.

$$\text{Also} \qquad \left[\mathbf{LS}, L^2\right] = \left[\mathbf{LS}, S^2\right] = \left[\mathbf{LS}, J^2\right] = [\mathbf{LS}, J_z] = 0. \tag{216}$$

$$\text{But} \qquad [\mathbf{LS}, L_z] \neq 0, \qquad \text{and} \qquad [\mathbf{LS}, S_z] \neq 0.$$

Both $|\ell s m_\ell m_s\rangle$ and $|\ell s j m\rangle$ are eigenfunctions of $\mathcal{H}_0$, however **LS** does not commute with L_z and S_z, which means that $|\ell s m_\ell m_s\rangle$ will not necessarily be an eigenfunction of **LS**.

The $|\ell s j m\rangle$ states are simultaneous **eigenfunctions** of L^2, S^2, J^2, J_z and **LS**, therefore the **coupled representation** is the one we should use because only diagonal matrix elements will appear in the secular determinant.

$$\begin{aligned}\langle \ell' s\, j' m'|\, \mathbf{LS}\, |\ell s j m\rangle &= \frac{1}{2}\langle \ell' s\, j' m'|\, (J^2 - L^2 - S^2)\, |\ell s j m\rangle \\ &= \frac{\hbar^2}{2}\Big[j(j+1) - \ell(\ell+1) - s(s+1)\Big]\delta_{j'j}\delta_{\ell'\ell}\delta_{m'm}.\end{aligned} \tag{217}$$

The expectation value of the radial function $\xi(r)$ is,

$$\langle n\ell|\, \xi(r)\, |n\ell\rangle = \int_0^\infty \xi(r) R^2_{n\ell}(r) r^2\, dr = \int_0^\infty \xi(r) u^2_{n\ell}(r)\, dr$$

$$= \frac{Ze^2}{2m^2c^2}\int_0^\infty \frac{1}{r^3} u^2_{n\ell}(r)\, dr = \frac{Ze^2}{2m^2c^2}\left\langle \frac{1}{r^3}\right\rangle = \frac{Ze^2}{2m^2c^2}\,\frac{Z^3}{a_0^3}\,\frac{1}{n^3(\ell+1)(\ell+\frac{1}{2})\ell}$$

Combining everything together,

$$\langle \ell s j m \,|\, \xi(r)\mathbf{LS} \,|\, \ell s j m \rangle = \frac{Z^4 e^2 \hbar^2}{4m^2c^2a_0^3} \frac{j(j+1) - \ell(\ell+1) - s(s+1)}{n^3(\ell+1)(\ell+\frac{1}{2})\ell}. \tag{218}$$

To simplify this take into account that

$$\alpha = \frac{e^2}{\hbar c}, \qquad a_0 = \frac{\hbar^2}{me^2} = \frac{\hbar}{\alpha mc}, \qquad \frac{1}{2}\alpha^2 mc^2 = -E_1^{(0)} = 1\,\mathrm{Ry}. \tag{219}$$

So

$$\frac{e^2\hbar^2}{4m^2c^2a_0^3} = \frac{e^2\hbar^2}{4m^2c^2} \frac{\alpha^3 m^3 c^3}{\hbar^3} = \frac{e^2}{\hbar c} \frac{\alpha^3 mc^2}{4}$$

$$= \frac{\alpha^4 mc^2}{4} = \left(\frac{1}{2}\alpha^2 mc^2\right) \frac{\alpha^2}{2} = \frac{\alpha^2}{2}\,\mathrm{Ry}. \tag{220}$$

Therefore in Rydberg units

$$E_{\rm so} = \frac{Z^4\alpha^2}{n^3}\,\frac{j(j+1)-\ell(\ell+1)-s(s+1)}{2\ell(\ell+\frac{1}{2})(\ell+1)}\ \ {\rm Ry}, \qquad ({\rm for}\ \ell\neq 0). \tag{221}$$

To get an expression valid in any system of units note that

$$E_n^{(0)} = -(Z^2/n^2)\,{\rm Ry}, \qquad E_n^{(0)} = -\frac{1}{2}\alpha^2 mc^2\frac{Z^2}{n^2}, \qquad (Z\alpha)^2 = -2n^2\frac{E_n^{(0)}}{mc^2}, \tag{222}$$

$$\frac{Z^4\alpha^2}{2n^3} = \frac{1}{2n}\frac{Z^2}{n^2}(Z\alpha)^2 = \frac{1}{2n}E_n^{(0)}\frac{2n^2E_n^{(0)}}{mc^2} = \frac{n}{mc^2}\left(E_n^{(0)}\right)^2. \tag{223}$$

So we can rewrite $E_{\rm so}$ as

$$E_{\rm so} = \frac{\left(E_n^{(0)}\right)^2}{mc^2}\,\frac{n[j(j+1)-\ell(\ell+1)-s(s+1)]}{\ell(\ell+\frac{1}{2})(\ell+1)}. \tag{224}$$

$$E_{\rm so} = -E_n^{(0)}\,(Z\alpha)^2\,\frac{j(j+1)-\ell(\ell+1)-s(s+1)}{2n\ell(\ell+\frac{1}{2})(\ell+1)}. \tag{225}$$

$$E_{\rm so} = \frac{Z^4\alpha^2}{n^3}\,\frac{j(j+1)-\ell(\ell+1)-s(s+1)}{2\ell(\ell+\frac{1}{2})(\ell+1)}\ \ {\rm Ry}, \qquad (\text{for } \ell \neq 0).$$

For $\ell = 0$ the previous formula is not applicable, but **LS** vanishes and $\langle 1/r^3 \rangle$ remains finite when *properly* computed. Therefore we are justified to conlude that, in any case, **the spin-orbit correction is zero for** $\ell = 0$.

We have $s(s+1) = 3/4$, therefore

$$j(j+1)-\ell(\ell+1)-s(s+1) = \begin{cases} \ell & \text{for } j = \ell + \frac{1}{2} \\ -(\ell+1) & \text{for } j = \ell - \frac{1}{2} \end{cases}$$

We can then rewrite $E_{\rm so}$ in Rydberg units as

$$E_{\ell+\frac{1}{2}} = \frac{Z^4\alpha^2}{n^3}\,\frac{\ell}{2\ell(\ell+\frac{1}{2})(\ell+1)}\ {\rm Ry}, \qquad E_{\ell-\frac{1}{2}} = -\frac{Z^4\alpha^2}{n^3}\,\frac{(\ell+1)}{2\ell(\ell+\frac{1}{2})(\ell+1)}\ {\rm Ry}$$

$$\Delta E_{\rm so} = E_{\ell+\frac{1}{2}} - E_{\ell-\frac{1}{2}} = \frac{Z^4\alpha^2}{n^3}\,\frac{1}{\ell(\ell+1)}\ {\rm Ry}.$$

In Rydberg units,

$$E_{\ell+\frac{1}{2}} = \frac{Z^4\alpha^2}{n^3}\,\frac{\ell}{2\ell(\ell+\frac{1}{2})(\ell+1)}\ \text{Ry}, \qquad E_{\ell-\frac{1}{2}} = -\frac{Z^4\alpha^2}{n^3}\,\frac{(\ell+1)}{2\ell(\ell+\frac{1}{2})(\ell+1)}\ \text{Ry}$$

$$\Delta E_{\text{so}} = E_{\ell+\frac{1}{2}} - E_{\ell-\frac{1}{2}} = \frac{Z^4\alpha^2}{n^3}\,\frac{1}{\ell(\ell+1)}\ \text{Ry}.$$

In arbitrary units,

$$E_{\ell+\frac{1}{2}} = \frac{\left(E_n^{(0)}\right)^2}{mc^2}\,\frac{n\ell}{\ell(\ell+\frac{1}{2})(\ell+1)}, \qquad E_{\ell-\frac{1}{2}} = -\frac{\left(E_n^{(0)}\right)^2}{mc^2}\,\frac{n(\ell+1)}{\ell(\ell+\frac{1}{2})(\ell+1)}$$

$$\Delta E_{\text{so}} = E_{\ell+\frac{1}{2}} - E_{\ell-\frac{1}{2}} = \frac{\left(E_n^{(0)}\right)^2}{mc^2}\,\frac{2n}{\ell(\ell+1)}.$$

The size of the spin-orbit energy shift in the Hydrogen atom is of the order of $10^{-5}\,\mathrm{eV}$, or $0.1\,\mathrm{cm}^{-1}$.

The energies between states with different values of the principal quantum number, n, are about $10^{4}\,\mathrm{cm}^{-1}$.

The spin-orbit energy increases rapidly with the atomic number due to the Z^4 dependence.

The conditions on j, ℓ and m for the spin-orbit interaction matrix elements to be nonzero can be read directly from the condition $\delta_{j'j}\delta_{\ell'\ell}\delta_{m'm}$ of equation (217).

$$\Delta j = \Delta \ell = \Delta m = \Delta(m_\ell + m_s) = 0. \tag{226}$$

To see if there are any restrictions on the individual values of m_ℓ and m_s we should compute the matrix elements of **LS** in the **uncoupled basis**, $|\ell s m_\ell m_s\rangle$.

To do this it is convenient to express **L** and **S** in spherical components,

$$L_{+1} = -\frac{1}{\sqrt{2}}(L_x + iL_y), \qquad L_{-1} = \frac{1}{\sqrt{2}}(L_x - iL_y), \qquad L_0 = L_z \tag{227}$$

$$S_{+1} = -\frac{1}{\sqrt{2}}(S_x + iS_y), \qquad S_{-1} = \frac{1}{\sqrt{2}}(S_x - iS_y), \qquad S_0 = S_z \tag{228}$$

$$L_x = -\frac{1}{\sqrt{2}}(L_{+1} - L_{-1}), \qquad L_y = \frac{i}{\sqrt{2}}(L_{+1} + L_{-1}), \qquad L_z = L_0 \tag{229}$$

$$S_x = -\frac{1}{\sqrt{2}}(S_{+1} - S_{-1}), \qquad S_y = \frac{i}{\sqrt{2}}(S_{+1} + S_{-1}), \qquad S_z = S_0 \tag{230}$$

This leads to $\mathbf{LS} = -L_{+1}S_{-1} + L_0S_0 - L_{-1}S_{+1}$, and therefore the matrix element

$$\langle \ell s m'_\ell m'_s \,|\, -L_{+1}S_{-1} + L_0S_0 - L_{-1}S_{+1} \,|\, \ell s m_\ell m_s \rangle \tag{231}$$

vanishes unless

$$\Delta m_\ell = 0, \pm 1 \qquad \Delta m_s = 0, \pm 1. \tag{232}$$

A further requirement is that, if m_ℓ increases by one unit, m_s must decrease by one unit and vice-versa.

As a reference, the different values of $\left\langle 1\tfrac{1}{2} m_\ell m_s \,\middle|\, \mathbf{LS} \,\middle|\, 1\tfrac{1}{2} m_\ell m_s \right\rangle$ are shown in the next table in units of $\hbar^2 \xi_{n\ell} = \hbar^2 \langle n\ell | \xi(r) | n\ell \rangle$.

$\left\langle 1\frac{1}{2} m_\ell m_s \right| \mathbf{LS} \left| 1\frac{1}{2} m_\ell m_s \right\rangle$ for p states in units of $\hbar^2 \xi_{n\ell} = \hbar^2 \langle n\ell | \xi(r) | n\ell \rangle$.

	$\left\vert 1\frac{1}{2} \right\rangle$	$\left\vert 1\,-\frac{1}{2} \right\rangle$	$\left\vert 0\frac{1}{2} \right\rangle$	$\left\vert 0\,-\frac{1}{2} \right\rangle$	$\left\vert -1\frac{1}{2} \right\rangle$	$\left\vert -1\,-\frac{1}{2} \right\rangle$
$\left\langle 1\frac{1}{2} \right\vert$	$\frac{1}{2}$					
$\left\langle 1\,-\frac{1}{2} \right\vert$		$-\frac{1}{2}$	$\frac{1}{\sqrt{2}}$			
$\left\langle 0\frac{1}{2} \right\vert$		$\frac{1}{\sqrt{2}}$	0			
$\left\langle 0\,-\frac{1}{2} \right\vert$				0	$\frac{1}{\sqrt{2}}$	
$\left\langle -1\frac{1}{2} \right\vert$				$\frac{1}{\sqrt{2}}$	$-\frac{1}{2}$	
$\left\langle -1\,-\frac{1}{2} \right\vert$						$\frac{1}{2}$

The notation in the table has been shortened from $|\ell s m_\ell m_s\rangle$ to $|m_\ell m_s\rangle$ because $\ell = 1$ and $s = 1/2$ for all the states in the table.

Relativistic correction to the kinetic energy.

The relativistic correction to the kinetic energy is given by

$$\mathcal{H}_r = -\frac{p^4}{8m^3c^2} = -\frac{1}{2mc^2}\left(\frac{p^2}{2m}\right)^2 . \tag{233}$$

Using $\mathcal{H}_0 = \frac{p^2}{2m} - \frac{Ze^2}{r}$ we have,

$$\mathcal{H}_r = -\frac{1}{2mc^2}\left(\mathcal{H}_0 + \frac{Ze^2}{r}\right)^2 = -\frac{1}{2mc^2}\left[\mathcal{H}_0^2 + Ze^2\left(\mathcal{H}_0\frac{1}{r} + \frac{1}{r}\mathcal{H}_0\right) + \frac{(Ze^2)^2}{r^2}\right].$$

We treat $\mathcal{H}_r$ as a perturbation and use the basis set $|n\ell sjm\rangle$ to compute the relevant matrix elements,

$$\langle n\,\ell' sj'm'|\mathcal{H}_r|n\ell sjm\rangle\,.$$

Let $E_n^{(0)}$ be an eigenvalue of $\mathcal{H}_0$, then

$$\left\langle n\ell' sj'm' \,\middle|\, \mathcal{H}_0^2 \,\middle|\, n\ell sjm\right\rangle = \left(E_n^{(0)}\right)^2 \delta_{\ell\ell'}\delta_{jj'}\delta_{mm'}\,. \tag{234}$$

Since $[\mathbf{p},\mathbf{r}] \neq 0$, $\mathcal{H}_0$ and $1/r$ **do not commute**

But, since $\mathcal{H}_0$ is Hermitian, $\langle \phi \,|\, \mathcal{H}_0 \,|\, \psi \rangle = \left\langle \mathcal{H}_0^\dagger \phi \,\middle|\, \psi \right\rangle = \langle \mathcal{H}_0 \phi \,|\, \psi \rangle$, we have

$$\left\langle n\,\ell' s j' m' \,\middle|\, \mathcal{H}_0 \frac{1}{r} \,\middle|\, n\ell s j m \right\rangle = \left\langle n\,\ell' s j' m' \,\middle|\, \frac{1}{r}\mathcal{H}_0 \,\middle|\, n\ell s j m \right\rangle$$

$$= E_n^{(0)} \left\langle n\,\ell' s j' m' \,\middle|\, \frac{1}{r} \,\middle|\, n\ell s j m \right\rangle = E_n^{(0)} \left\langle \frac{1}{r} \right\rangle \delta_{\ell\ell'}\delta_{jj'}\delta_{mm'}.$$

where $\langle 1/r \rangle$ only depends on the radial part of the wave function and is independent of ℓ, j, m. We have also

$$\left\langle n\,\ell' s j' m' \,\middle|\, \frac{1}{r^2} \,\middle|\, n\ell s j m \right\rangle = \left\langle \frac{1}{r^2} \right\rangle \delta_{\ell\ell'}\delta_{jj'}\delta_{mm'}. \tag{235}$$

Therefore $\mathcal{H}_r$ has only diagonal matrix elements and

$$\mathcal{H}_r = -\frac{1}{2mc^2}\left[\mathcal{H}_0^2 + Ze^2\left(\mathcal{H}_0\frac{1}{r} + \frac{1}{r}\mathcal{H}_0\right) + \frac{(Ze^2)^2}{r^2}\right].$$

$$\langle \mathcal{H}_r \rangle = -\frac{E_n^{(0)}}{2mc^2}\left[E_n^{(0)} + 2Ze^2\left\langle \frac{1}{r} \right\rangle + \frac{(Ze^2)^2}{E_n^{(0)}}\left\langle \frac{1}{r^2} \right\rangle\right]. \tag{236}$$

For Hydrogen we have

$$E_n^{(0)} = -\frac{Z^2}{n^2}\frac{e^2}{2a_0} = -\frac{Z^2}{n^2}\frac{me^4}{2\hbar^2} = -\frac{Z^2}{n^2}\,\mathrm{Ry},$$

and

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a_0}\frac{1}{n^2}, \qquad \left\langle \frac{1}{r^2} \right\rangle = \frac{Z^2}{a_0^2}\frac{1}{n^3(\ell+\frac{1}{2})}. \tag{237}$$

$$\langle \mathcal{H}_r \rangle = -\frac{E_n^{(0)}}{2mc^2}\left[-\frac{Z^2}{n^2}\frac{e^2}{2a_0} + 2Ze^2\frac{Z}{a_0}\frac{1}{n^2} - \frac{n^2}{Z^2}\frac{2a_0}{e^2}(Ze^2)^2\frac{Z^2}{a_0^2}\frac{1}{n^3(\ell+\frac{1}{2})}\right]$$

$$= -\frac{E_n^{(0)}Z^2e^2}{mc^2a_0}\left[-\frac{1}{4n^2} + \frac{1}{n^2} - \frac{1}{n(\ell+\frac{1}{2})}\right] = E_n^{(0)}Z^2\alpha^2\left[-\frac{3}{4n^2} + \frac{1}{n(\ell+\frac{1}{2})}\right],$$

where

$$\alpha^2 = \left(\frac{e^2}{\hbar c}\right)^2 = \frac{e^2}{mc^2a_0}, \qquad a_0 = \frac{\hbar^2}{me^2}.$$

This formula for $\langle \mathcal{H}_r \rangle$ **is valid for all values of** ℓ

$$E_{\rm r} = \langle \mathcal{H}_r \rangle = E_n^{(0)} \frac{(Z\alpha)^2}{n} \left[-\frac{3}{4n} + \frac{1}{(\ell + \frac{1}{2})} \right]. \tag{238}$$

To write it in Rydberg units note that $E_n^{(0)} = -(Z^2/n^2)$ Ry, therefore

$$E_{\rm r} = -\frac{Z^4\alpha^2}{n^3} \left[-\frac{3}{4n} + \frac{1}{(\ell + \frac{1}{2})} \right] \text{ Ry} \tag{239}$$

Using the relations

$$E_n^{(0)} = -\frac{1}{2}\alpha^2 mc^2 \frac{Z^2}{n^2}, \qquad \frac{Z^2}{n^2} = -\frac{2E_n^{(0)}}{\alpha^2 mc^2}, \tag{240}$$

we can also write the relativistic correction in this useful form

$$E_{\rm r} = \frac{E_n^{(0)} Z^2\alpha^2}{4n^2} \left(\frac{4n}{\ell + \frac{1}{2}} - 3 \right) = -\frac{2\left(E_n^{(0)}\right)^2 \alpha^2}{4\alpha^2 mc^2} \left(\frac{4n}{\ell + \frac{1}{2}} - 3 \right)$$

$$E_{\rm r} = -\frac{\left(E_n^{(0)}\right)^2}{2mc^2} \left(\frac{4n}{\ell + \frac{1}{2}} - 3 \right) \tag{241}$$

The Darwin term.

For the Darwin term let's consider $\mathbf{E} = -\boldsymbol{\nabla}\phi$, with $\phi = Ze/r$. Then[2]

$$\mathcal{H}_{\mathrm{D}} = \frac{e\hbar^2}{8m^2c^2}\boldsymbol{\nabla}\cdot\mathbf{E} = -\frac{Ze^2\hbar^2}{8m^2c^2}\nabla^2\left(\frac{1}{r}\right) = \frac{4\pi Ze^2\hbar^2}{8m^2c^2}\delta(\mathbf{r}). \tag{242}$$

We need only to consider the radial part of the wave function.
We have $\langle n\ell|\delta(\mathbf{r})|n\ell\rangle = |\psi(0)|^2$ so

$$\langle\mathcal{H}_{\mathrm{D}}\rangle = \frac{\pi Ze^2\hbar^2}{2m^2c^2}|\psi(0)|^2 = E_{\mathrm{D}}. \tag{243}$$

This formula implies that $\langle\mathcal{H}_{\mathrm{D}}\rangle$ is nonzero only for s states. In Hydrogen

$$|\psi(0)|^2 = \frac{Z^3}{\pi n^3 a_0^3}, \qquad E_{\mathrm{D}} = \frac{\pi Ze^2\hbar^2}{2m^2c^2}\frac{Z^3}{\pi n^3 a_0^3} = \frac{Z^4e^2\hbar^2}{2n^3m^2c^2a_0^3}. \tag{244}$$

[2] Remember that $\nabla^2(1/r) = -4\pi\delta(\mathbf{r})$.

In Rydberg units,

$$E_{\rm D} = \frac{Z^4\alpha^2}{n^3}\ {\rm Ry}, \qquad (\ell = 0 \ \text{ only}) \tag{245}$$

Since $E_n^{(0)} = -(Z^2/n^2)\ {\rm Ry}$, we can also write

$$E_{\rm D} = -E_n^{(0)}\frac{(Z\alpha)^2}{n}, \qquad (\ell = 0 \ \text{ only}). \tag{246}$$

To make the comparison with mc^2 explicit we can trade $(Z\alpha)^2$ for another factor of $E_n^{(0)}$ using the relation $E_n^{(0)} = -\frac{1}{2}\alpha^2 mc^2\frac{Z^2}{n^2}$. Therefore

$$E_{\rm D} = 2n\frac{\left(E_n^{(0)}\right)^2}{mc^2}. \tag{247}$$

Combining all corrections.

The corrections due to the spin-orbit effect and the Darwin term are

$$E_{\rm so} = \frac{Z^4\alpha^2}{n^3}\,\frac{j(j+1)-\ell(\ell+1)-s(s+1)}{2\ell(\ell+\frac{1}{2})(\ell+1)}\ {\rm Ry}, \qquad E_{\rm D} = \frac{Z^4\alpha^2}{n^3}\ {\rm Ry}. \tag{248}$$

The expression for $E_{\rm so}$ is only valid for $\ell \neq 0$, although we know that $E_{\rm so} = 0$ for states with $\ell = 0$ anyhow. On the contrary, the Darwin correction applies only to states with $\ell = 0$. The relativistic correction is valid for all values of ℓ,

$$E_{\rm r} = -\frac{Z^4\alpha^2}{n^3}\left[\frac{1}{(\ell+\frac{1}{2})} - \frac{3}{4n}\right]\ {\rm Ry}. \tag{249}$$

Taking all this into account, by adding the three corrections we obtain a formula that depends only on n and j, but not on ℓ or m.

$$E_{\rm so} + E_{\rm r} + E_{\rm D} = -\frac{Z^4\alpha^2}{n^3}\left[\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right]\ {\rm Ry}. \tag{250}$$

The zero-order Hydrogen energy levels are given by $E_n^{(0)} = -(Z^2/n^2)$ Ry. By including all corrections we have computed we arrive then at

$$E_{nj} = -\frac{Z^2}{n^2}\left[1 + \frac{Z^2\alpha^2}{n}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right)\right] \text{ Ry.} \tag{251}$$

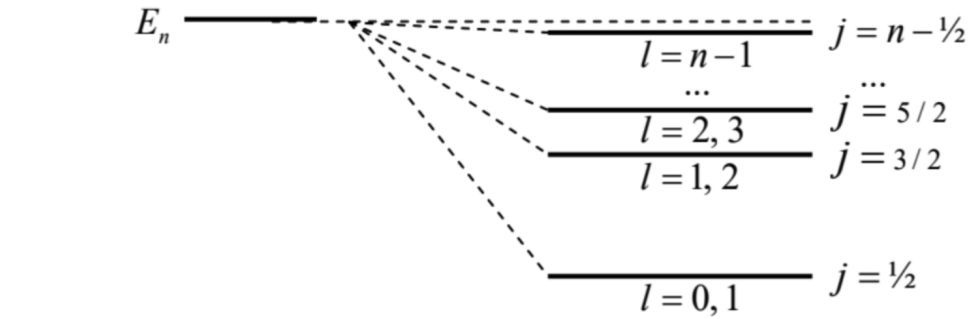
In arbitrary units,

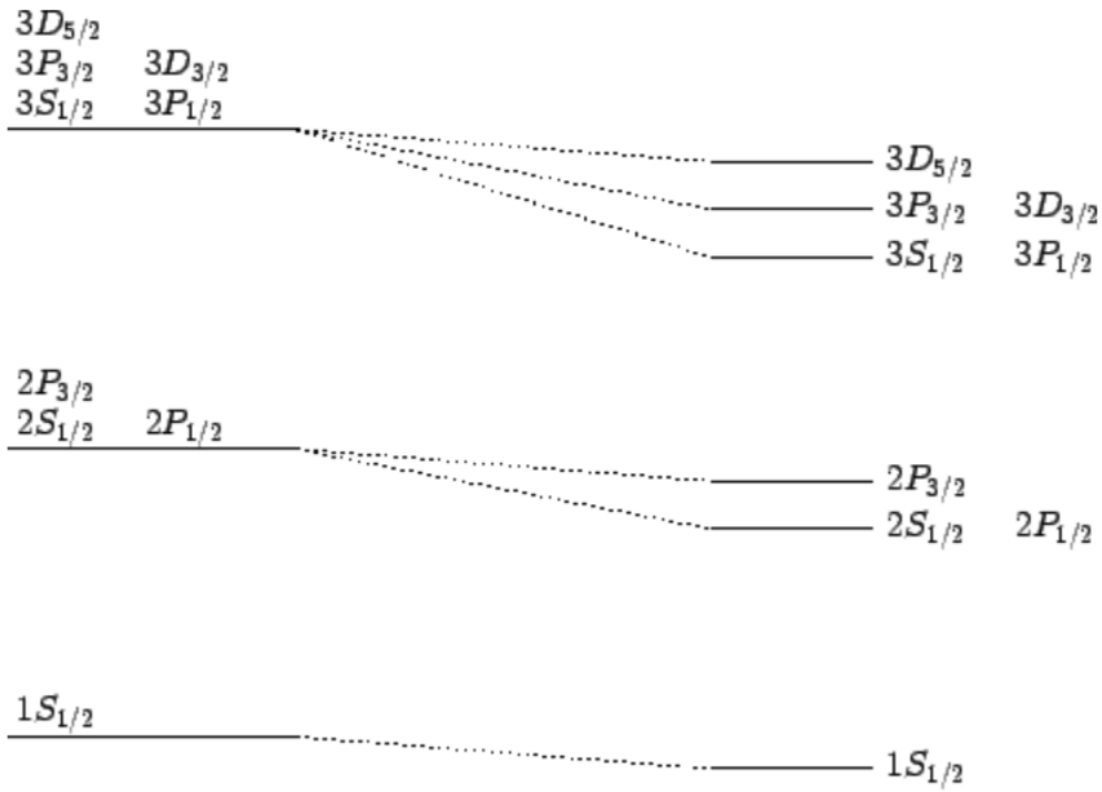
$$E_{nj} = E_n^{(0)}\left[1 + \frac{Z^2\alpha^2}{n}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right)\right]. \tag{252}$$

After relativistic corrections, each E_n energy level splits into n different levels, one for each possible value of j in the list: $j = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \ldots, n - \frac{1}{2}$.

This is called **fine structure splitting**.

The dimensionless fine structure constant, $\alpha \approx \dfrac{1}{137}$, controls the scale of the splitting.


E_n
$j = n - ½$
$l = n-1$
...
...
$j = 5/2$
$l = 2, 3$
$j = 3/2$
$l = 1, 2$
$j = ½$
$l = 0, 1$


$3D_{5/2}$
$3P_{3/2}$ $3D_{3/2}$
$3S_{1/2}$ $3P_{1/2}$
$3D_{5/2}$
$3P_{3/2}$ $3D_{3/2}$
$3S_{1/2}$ $3P_{1/2}$
$2P_{3/2}$
$2S_{1/2}$ $2P_{1/2}$
$2P_{3/2}$
$2S_{1/2}$ $2P_{1/2}$
$1S_{1/2}$
$1S_{1/2}$

The Lamb shift.

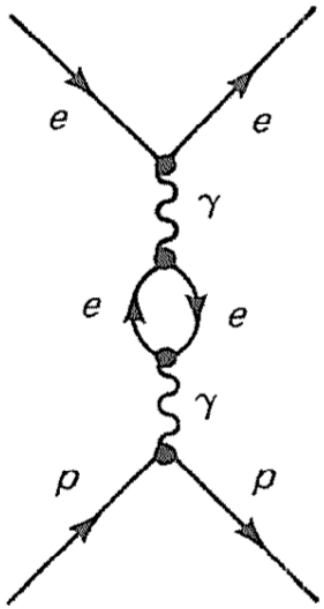
$$E_{nj} = E_n^{(0)} \left[1 + \frac{Z^2\alpha^2}{n} \left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n} \right) \right]. \tag{253}$$

This formula predicts the energies of the $^2\mathrm{S}_{1/2}$ and $^2\mathrm{P}_{1/2}$ hydrogen levels (notation $^{2s+1}\mathrm{L}_j$) to be the same for a given n.

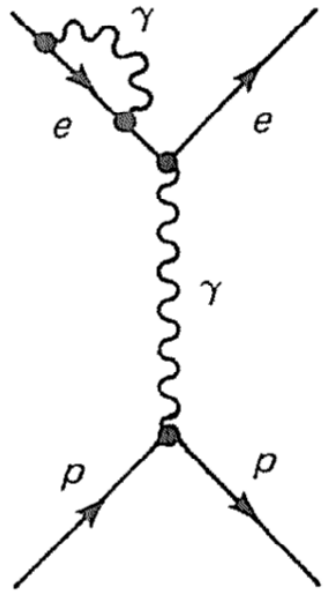
This is a result which holds even for the exact solution of the Dirac equation for Hydrogen, which predicts that states with the same value of the quantum number j, but different values of ℓ, have the same energy.

In fact there is a slight upward shift of the $^2\mathrm{S}_{1/2}$ level with respect to $^2\mathrm{P}_{1/2}$.

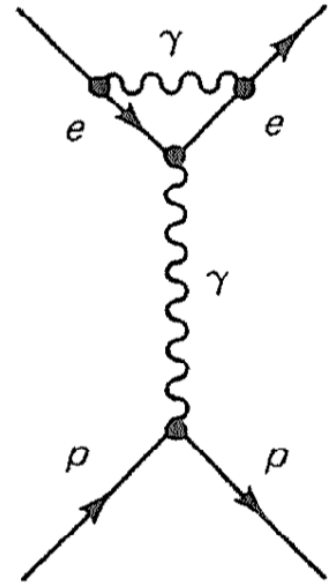
This is due to the quantum nature of the electromagnetic field. In all precedent calculations the electromagnetic field has been treated as a classical field, but to explain the Lamb shift we would need to quantize it (use quantum electrodynamics).



Vacuum polarization



Electron mass renormalization



Anomalous magnetic moment

Some loop diagrams contributing to the Lamb shift.

For $\ell = 0$ the Lamb shift has been computed to be

$$\Delta E_{\text{Lamb}} = \alpha^5 mc^2 \frac{1}{4n^3} k(n,0), \tag{254}$$

where $k(n,0)$ is a numerical factor that varies slightly with n, from 12.7 for $n = 1$ to 13.2 for $n \to \infty$. For $\ell \neq 0$ the Lamb shift is

$$\Delta E_{\text{Lamb}} = \alpha^5 mc^2 \frac{1}{4n^3} \left[k(n,\ell) \pm \frac{1}{\pi(j+\frac{1}{2})(\ell+\frac{1}{2})} \right] \quad \text{for} \quad j = \ell \pm \frac{1}{2}, \tag{255}$$

where $k(n,\ell)$ is a very small number (less than 0.05) that varies slightly with n and ℓ. The Lamb shift is very small (about 4.35×10^{-5} eV for the $^2S_{1/2}$ - $^2P_{3/2}$ energy difference). For s states it is about $1/10$ of the size of the fine structure.

The hierarchy of corrections to the (Bohr) Hydrogen energy levels is the following

Bohr energies:	of order	$\alpha^2 mc^2$
Fine structure:	of order	$\alpha^4 mc^2$
Lamb shift:	of order	$\alpha^5 mc^2$
Hyperfine splitting:	of order	$(m/m_p)\alpha^4 mc^2$

The hyperfine splitting is smaller than the Lamb shift by an order of magnitude due to the small value of the electron/proton mass ratio.

Antihydrogen.

The antihydrogen is a $\overline{\mathrm{p}}\mathrm{e}^+$ bound system. It is specially interesting to study possible fundamental differences between matter and antimatter.

First produced at CERN's Antiproton Decelerator (AD) in 1996.

A recent publication of the ALPHA collaboration has reported the observation of the 1S-2S transition in trapped antihydrogen atoms.

One of the goals is to measure the frequency of the 1S-2S transition in antihydrogen and compare it with the very precise measured valued in hydrogen, 2466061413187035(10) Hz.

A significant deviation from this value would mean a breakdown of CPT symmetry, but no anomaly has been observed so far.

Positronium and muonium.

The positronium is a $\mathrm{e}^+\mathrm{e}^-$ bound system. It has a reduced mass of

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{m_e}{2} \tag{256}$$

The unperturbed Bohr energies are given by half of the formula we derived for hydrogen,

$$E_n^{\mathrm{pos}} = \frac{1}{2} E_n = -\alpha^2 mc^2 \frac{1}{4n^2}. \tag{257}$$

Bohr radius a factor of 2 larger: $a_0^{\mathrm{pos}} = 2a_0 = 1.06 \times 10^{-8}\,\mathrm{cm}$.

Perturbative corrections get similar factors, except the hyperfine splitting, which is of the same order than the fine structure because there is no mass suppression ratio m_e/m_p.

The positronioum decays to two photons with a lifetime of

$$\tau = \frac{2\hbar}{\alpha^5 mc^2} = 1.25 \times 10^{-10}\,\mathrm{sec}. \tag{258}$$

The muonium is a $\mu^+\mathrm{e}^-$ bound system. $m_\mu \approx 207 m_e$. The lifetime of the muonium is 2.2×10^{-6} seconds, which is the lifetime of the muon itself.

Rydberg atoms.

An atom with an electron in a very high-energy state, with principal quantum number even as high as $n = 100$, is called a Rydberg atom.

The size of such an atom is enormous, with electron orbital radii of the order of 10^{-7} m, almost as big as a bacteria.

The ionization energy for hydrogen atoms with $n = 100$ is very small, on 1.36×10^{-3} eV.

The energy separation for states around $n = 100$ is also very small, since we are approaching the region were the spectrum becomes continuum.

The study of Rydberg atoms is important for several areas of astrophysics, plasma physics and quantum optics.

In the interstellar vacuum space a Rydberg atom can in principle have a long lifetime and emit radio waves which can be detected on earth by radio telescopes.

Pionium.

The pionium is a $\pi^+\pi^-$ bound system, called usually $A_{2\pi}$.

Reduced mass $m_\pi/2$ ($m_\pi = 139.57\,\mathrm{MeV}/c^2$), leading to a Bohr radius of $378\,\mathrm{fm} = 3.78 \times 10^{-13}\,\mathrm{m}$.

This *exotic atom* is very unstable, it decays mainly from the $1s$ state to two neutral pions, $A_{2\pi} \to \pi^0 + \pi^0$, with a lifetime of the order of 10^{-15} seconds.

The measurement of the $A_{2\pi}$ decay width to two neutral pions, $\Gamma_{2\pi^0}$, is an important input to understand quantum chromodynamics (QCD) at low energy.

$A_{2\pi}$ atoms studied by the DIRAC (Dimeson Relativistic Atom Complex) collaboration at CERN.

Protons accelerated up to $24\,\mathrm{GeV}/c$ by the CERN PS accelerator directed into thin target foils of less than $100\ \mu\mathrm{m}$ thickness. The proton collision with the target produces many particles, most of them pions, which can form $A_{2\pi}$ atoms.

These atoms travel inside the target foil interacting with the ordinary atoms of the target. This may lead to the break up (ionization) of the $A_{2\pi}$ atom before it has had time to decay to $2\pi^0$.

By measuring the momentum spectra of pairs of oppositely charged pions leaving the target foil it is possible to infer the ionization probability and the $\Gamma_{2\pi^0}$ decay width.

Quarkonium.

In the quark model all mesons are bound states of two quarks, $\mathrm{q_1 q_2}$. The light-quark mesons, like for example the π^0, which is a combination of $\mathrm{u\bar{u}}$ and $\mathrm{d\bar{d}}$ states, are intrinsically relativistic and a simple analysis is not possible.

Heavy-quark mesons, however, like the J/ψ ($\mathrm{c\bar{c}}$) or the η_b ($\mathrm{b\bar{b}}$), could be possible candidates. Even in these systems the interaction energy, E, is so large that the different energy levels are treated as *different particles*, with masses given by

$$M = m_1 + m_2 + \frac{E}{c^2} \tag{259}$$

pause The binding is due to the strong force. The potential could in principle be derived from quantum chromodynamics (QCD), but nobody has been able to do it yet.

The strong potential at short distances (but not very short) goes like $1/r$, as in the Coulomb case. For large distances the potential may be taken to be linear with r, so a possible parametrization could be

$$V(r) = -\frac{4}{3}\frac{\alpha_s \hbar c}{r} + F_0 r, \tag{260}$$

where α_s is the chromodynamic analog to the fine structure constant. The constant F_0 is chosen to fit the experimental data and the result is about 900 MeV fm^{-1}. This is $14 \times 10^4\,\mathrm{J/m} = 140000\,\mathrm{N}$, which would mean that a quark and an antiquark attract one another with a force capable to lift 14 tons.

Quarks cannot be found as free particles outside hadrons. If enough energy is put into a $\mathrm{q\bar{q}}$ system, a new pair of bound quarks is formed instead of tearing apart the old one.