Clebsch–Gordan Coefficients

When a system has a total angular momentum that arises from the addition of two individual angular momenta, the system's angular momentum quantum states can be expanded into the TAM basis (page 83) or the TP basis (page 82). **Clebsch-Gordan (CG) coefficients**, described below, are the superposition coefficients of the expansion of an element of one of these bases into the other basis. The CG coefficient tables on pages 118–121 provide these coefficients for angular momentum quantum numbers $1/2 \leq j_1 \leq 2$ and $1/2 \leq j_2 \leq j_1$ where $j_1 \geq j_2$.

The notation below follows that of pages 82–83 and assumes the convention $j_1 \geq j_2$ usually adopted for the tabulation of CG coefficients. For brevity, the quantum numbers j_1 and j_2 are often omitted from the TAM kets and bras.

For two individual angular momenta with quantum numbers j_1 and j_2, the expansion of a TP basis element into the TAM basis is written (using a closure relation) as

$$|j_1, j_2, m_1, m_2\rangle = \sum_{J=|j_1-j_2|}^{j_1+j_2} \sum_{m_J=-J}^{J} \langle J, m_J|j_1, j_2, m_1, m_2\rangle |J, m_J\rangle$$

where $\langle J, m_J|j_1, j_2, m_1, m_2\rangle$ is a CG coefficient. The expansion of a TAM basis element into the TP basis is written as

$$|J, m_J\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} \langle j_1, j_2, m_1, m_2|J, m_J\rangle |j_1, j_2, m_1, m_2\rangle$$

By convention, the CG coefficients are defined to be real, so that $\langle j_1, j_2, m_1, m_2|J, m_J\rangle = \langle J, m_J|j_1, j_2, m_1, m_2\rangle$.

Note the following:

- For the case $J = j_1 + j_2$:
  $\langle J, m_J = J|j_1, j_2, m_1 = j_1, m_2 = j_2\rangle = 1$
- Also for $J = j_1 + j_2$:
  $\langle J, m_J = -J|j_1, j_2, m_1 = -j_1, m_2 = -j_2\rangle = 1$
- If $m_1 + m_2 \neq m_J$, then $\langle J, m_J|j_1, j_2, m_1, m_2\rangle = 0$

Clebsch–Gordan Coefficients: Usage

When merging the state spaces of two systems characterized by angular momentum quantum numbers j_1 and j_2, the steps below are used to determine the associated CG coefficients using the tables given on pages 118–121. As is done on pages 84–86, the quantum numbers j_1 and j_2 are omitted from the row and column labels (explained below) in a given CG table because they are associated with every ket in the given table. CG coefficient tables are used as follows:

1. Identify the relevant tabular group. The two numbers in the upper-left corner of each grouping of tables are j_1 and j_2, with j_1 assumed to be the larger of the two values if they are not equal.

2. Within a table, the column labels are J and m_J (J is above m_J). The row labels are m_1 and m_2 (m_1 is to the left of m_2). Note the order of m_1 and m_2: m_1 is associated with j_1, the larger of the two angular momenta.

3. Every number (on a white background) in the tables is associated with a pair of values (J, m_J) given by the column label above that number and a pair of values (m_1, m_2) given by the row label to the left of that number. The CG coefficient is the square root of that number within the table, with any minus sign (if present) placed outside of the radical.

4. Using the steps described above, the expansion of a TAM basis element $|J, m_J\rangle$ into the TP basis involves reading a column of numbers in the column headed by J and m_J. Each CG coefficient is the coefficient for the associated TP basis element $|m_1, m_2\rangle$ in the superposition. All coefficients are zero for which there is not a corresponding pair of m_1 and m_2 row labels within that section of the table; such is the case if $m_J \neq m_1 + m_2$. Similarly, the expansion of a TP basis element into the TAM basis involves reading a row of numbers to the right of the relevant m_1 and m_2 labels.

Clebsch–Gordan Coefficients: Examples

The following examples incorporate the rules for addition of angular momentum given on pages 83–87 and the usage of the CG coefficient tables on pages 118–121. The examples are based on the addition of two spins $s_1 = 3/2$ and $s_2 = 1/2$, following the example and table given on page 84.

Example 1: The ket $|s_1 = 3/2, s_2 = 1/2, m_1 = -3/2, m_2 = 1/2\rangle$ is compactly written $|m_1 = -3/2, m_2 = 1/2\rangle$ by omitting the quantum numbers s_1 and s_2 from all kets and bras below. To expand this TP basis state into the TAM basis $\{|S, m_S\rangle\}$, the $\frac{3}{2} \times \frac{1}{2}$ CG coefficient table on page 118 is used. Since $m_S = m_1 + m_2 = -1$ (for this case), the only elements of the superposition with non-zero coefficients are $|S = 2, m_s = -1\rangle$ and $|S = 1, m_s = -1\rangle$.

The coefficients are determined by the numbers to the right of the row labels $-3/2$ (left) and $+1/2$ (right). The number 1/4 is found in the column headed by 2 (above) and -1 (below). This column corresponds to the TAM state $|S = 2, m_S = -1\rangle$, and the corresponding CG coefficient is $\sqrt{1/4}$. The number $-3/4$ is found in the column headed by 1 (above) and -1 (below). This column corresponds to the TAM state $|S = 1, m_S = -1\rangle$, and the corresponding CG coefficient is $-\sqrt{3/4}$. The expansion of $|m_1 = -3/2, m_2 = 1/2\rangle$ into the TAM basis is then written as

$$|m_1 = -\frac{3}{2}, m_2 = \frac{1}{2}\rangle = \sqrt{\frac{1}{4}}|S = 2, m_S = -1\rangle - \sqrt{\frac{3}{4}}|S = 1, m_S = -1\rangle$$

Example 2: Expanding a TAM basis state into the TP basis is similar to the above example, but the numbers in a column (rather than a row) of a section of the table determine the expansion coefficients. For $s_1 = 3/2$ and $s_2 = 1/2$, the TAM state $|S = 1, m_S = 1\rangle$ is written in the TP basis as

$$|S = 1, m_S = 1\rangle = \sqrt{\frac{3}{4}}|m_1 = \frac{3}{2}, m_2 = -\frac{1}{2}\rangle - \sqrt{\frac{1}{4}}|m_1 = \frac{1}{2}, m_2 = \frac{1}{2}\rangle$$

Note that the sum of the squares of the CG coefficients in the expansion of any state into another basis must equal 1.

normalization

no exact solution   CTXI

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Stationary Perturbation Theory

Stationary perturbation theory (SPT) constructs approximate energy eigenvalues and eigenstates of a time-independent Hamiltonian $\hat{H} = \hat{H}_0 + \lambda\hat{W}$, for which

- $\hat{H}_0|\varphi_n^i\rangle = E_n^0|\varphi_n^i\rangle$, where all E_n^0 and $|\varphi_n^i\rangle$ are known. For each eigenvalue E_n^0, the superscript i accounts for degeneracy, $i \in \{1, 2, \ldots, g_n\}$.

- λ is a positive or negative real scalar, $|\lambda| \ll 1$

lam=w/wo - $\lambda\hat{W}$ is a small perturbation, meaning that the matrix elements of $\lambda\hat{W}$ are much smaller in magnitude than the differences between the eigenvalues of $\hat{H}_0$.

- The eigenvalues and eigenstates of $\hat{H}$ are defined by $\hat{H}|\psi_{n,j}\rangle = E_{n,j}|\psi_{n,j}\rangle$. For a given n, the eigenvalues $\{E_{n,j}\}$ and eigenstates $\{|\psi_{n,j}\rangle\}$ may be different than the associated unperturbed quantities E_n^0 and $\{|\varphi_n^i\rangle\}$, where $i, j \in \{1, 2, \ldots, g_n\}$. The index j labels the different solu-
w degeneracy tions to the eigenvalue equation for $\hat{H}$ in cases where
aslam increases $g_n > 1$. The indices i and j associated with a given n may
they may get be omitted if $g_n = 1$.
dispersed
(no degeneracy) goal -> H(lam)|psi_n,j(lam)>=E_n,j(lam)|psi_n,j(lam)>, j in{1,...,gn}
Non-degenerate SPT is used to find approximate solutions to the eigenvalue equation for $\hat{H}$ for a given n when there is no degeneracy in the $\hat{H}_0$ eigenvalue E_n^0 (i.e., $g_n = 1$). $\hat{H}_0$ may have degeneracies associated with other eigenvalues E_p^0, where $p \neq n$. Solutions are expanded as power series in λ.

The non-degenerate SPT solutions to second order in λ for E_n and to first order in λ for $|\psi_n\rangle$ are

$$E_n \approx E_n^0 + \lambda\langle\varphi_n|\hat{W}|\varphi_n\rangle + \lambda^2 \sum_{p \neq n} \sum_{i=1}^{g_p} \frac{|\langle\varphi_p^i|\hat{W}|\varphi_n\rangle|^2}{E_n^0 - E_p^0}$$
diagonal elements

$$|\psi_n\rangle \approx |\varphi_n\rangle + \lambda \sum_{p \neq n} \sum_{i=1}^{g_p} \frac{\langle\varphi_p^i|\hat{W}|\varphi_n\rangle}{E_n^0 - E_p^0}|\varphi_p^i\rangle$$

The approximate $|\psi_n\rangle$ must be then be normalized. Expansions to first order in λ for E_n and to zeroth order in λ for $|\psi_n\rangle$ are obtained by omitting the double-summation terms in the two expressions above.

Degenerate Stationary Perturbation Theory

Degenerate SPT applies SPT (page 90) to treat a g_n-fold degeneracy ($g_n > 1$) in an unperturbed eigenvalue E_n^0 of $\hat{H}_0$. As with the non-degenerate case, solutions to the eigenvalue equation for $\hat{H}$ are expressed as power series in λ. Solutions to first order in λ for the eigenvalues of $\hat{H}$ and to zeroth order in λ for the eigenstates are described below. In this limit, the g_n eigenstates $\{|\psi_{n,j}\rangle\}$ of $\hat{H}$ that are associated with eigenvalues $\{E_{n,j}\}$ are found to be superpositions of the g_n degenerate eigenstates $\{|\varphi_n^i\rangle\}$ of $\hat{H}_0$, with $i, j \in \{1, 2, \ldots, g_n\}$. Some or all of these degeneracies may be removed when the perturbation is present. Given specific values of n and g_n, solutions to first order in λ for the set $\{E_{n,j}\}$ and to zeroth order in λ for the set $\{|\psi_{n,j}\rangle\}$ are obtained by the following steps:

1. Given a state space $\mathcal{E}$, identify the subspace $\mathcal{E}_n$ that is spanned by the degenerate state vectors $\{|\varphi_n^i\rangle\}$, with $i \in \{1, 2, \ldots, g_n\}$.

2. Define $\hat{H}_0^{(n)}$ and $\lambda \hat{W}^{(n)}$ as the unperturbed Hamiltonian and the perturbation that act within subspace $\mathcal{E}_n$. The Hamiltonian acting within this subspace is then $\hat{H}^{(n)} = \hat{H}_0^{(n)} + \lambda \hat{W}^{(n)}$.

3. Find the g_n eigenstates and eigenvalues of $\hat{W}^{(n)}$; that is, solve the eigenvalue equation

$$\hat{W}^{(n)}|v_{n,j}\rangle = \epsilon_{n,j}|v_{n,j}\rangle$$

This step is performed by first constructing the $g_n \times g_n$ matrix that represents $\hat{W}^{(n)}$ in the representation defined by the basis $\{|\varphi_n^1\rangle, |\varphi_n^2\rangle, \ldots, |\varphi_n^{g_n}\rangle\}$ that spans the subspace $\mathcal{E}_n$. The matrix elements are given by $W_{pq}^{(n)} = \langle \varphi_n^p | \hat{W}^{(n)} | \varphi_n^q \rangle$ ($p, q \in \{1, 2, \ldots, g_n\}$).

Results: The eigenvalues (to first order in λ) and eigenstates (to zeroth order in λ) of $\hat{H}$ that are associated with the unperturbed energy eigenvalue E_n^0 are

$$E_{n,j} \approx E_n^0 + \lambda \epsilon_{n,j}$$

$$|\psi_{n,j}\rangle \approx |v_{n,j}\rangle$$

Time-Dependent Perturbation Theory

Time-dependent perturbation theory (TDPT) is used to find an approximate time-dependent expansion of a quantum state $|\Psi(t)\rangle$ into a known basis; the basis states are the eigenstates of a time-independent Hamiltonian $\hat{H}_0$ but not eigenstates of the full time-dependent system Hamiltonian $\hat{H}(t)$. TDPT is commonly used to find the approximate time-dependent probability $\mathcal{P}(t)$ of measuring that a transition has occurred from some known initial state to some specified final state. The system Hamiltonian is given by $\hat{H}(t) = \hat{H}_0 + \lambda\hat{W}(t)$ for which

- $\hat{H}_0|\varphi_n\rangle = E_n|\varphi_n\rangle$, where all E_n and $|\varphi_n\rangle$ are known. The index n may be a compound index representing a set of quantum numbers, including indices that indicate energy degeneracy.

- λ is a positive or negative real scalar, $|\lambda| \ll 1$

- $\lambda\hat{W}(t)$ is a weak perturbation, or timescales of interest are short enough, so that $\mathcal{P}(t) \ll 1$

- $|\Psi(t)\rangle$ is expanded into the $\{|\varphi_n\rangle\}$ basis as follows:

$$|\Psi(t)\rangle = \sum_n c_n(t)|\varphi_n\rangle = \sum_n b_n(t)e^{-iE_n(t-t_0)/\hbar}|\varphi_n\rangle$$

  where the terms $b_n(t) = c_n(t)e^{iE_n(t-t_0)/\hbar}$ are the expansion coefficients in the interaction picture (page 46)

- Each interaction-picture coefficient $b_n(t)$ is expanded in powers of λ: $b_n(t) = b_n^{(0)} + \lambda b_n^{(1)}(t) + \cdots + \lambda^r b_n^{(r)}(t) + \cdots$, where $b_n^{(r)}(t)$ is the rth-order coefficient in the expansion of $|\varphi_n\rangle$, $b_n^{(0)} = b_n(t_0)$ is the expansion coefficient of $|\varphi_n\rangle$ for the initial initial state $|\Psi(t_0)\rangle$, and $b_n^{(r)}(t_0) = 0$ for $r > 0$ for every n

---

The TDPT solution for the rth-order term $(r > 0)$ is

$$\lambda^r b_n^{(r)}(t) = \frac{\lambda^r}{i\hbar}\int_{t_0}^t \sum_k dt'\, e^{i\omega_{nk}t'} W_{nk}(t') b_k^{(r-1)}(t')$$

where $\omega_{nk} \equiv \frac{E_n - E_k}{\hbar}$ and $W_{nk}(t') = \langle\varphi_n|\hat{W}(t')|\varphi_k\rangle$.

TDPT: First-Order Solution

The **first-order transition probability** $\mathcal{P}_{if}^{(1)}$ from a known initial eigenstate $|\varphi_i\rangle$ of $\hat{H}_0$ to a final eigenstate $|\varphi_f\rangle$ of $\hat{H}_0$ is determined by first specifying the initial condition at time t_0: $|\Psi(t_0)\rangle = |\varphi_i\rangle$, so that $b_n^{(0)} = \delta_{ni}$ (Kronecker delta) for each n.

The first-order term in the expansion of $b_n(t)$ $(n \neq i)$ is

$$\lambda b_n^{(1)}(t) = \frac{\lambda}{i\hbar} \int_{t_0}^{t} dt' \, e^{i\omega_{ni}t'} W_{ni}(t')$$

The time-dependent transition probability $\mathcal{P}_{if}(t)$ from the initial state $|\Psi(t_0)\rangle = |\varphi_i\rangle$ to $|\Psi(t)\rangle = |\varphi_f\rangle$ $(f \neq i)$ is then approximated as $\mathcal{P}_{if}^{(1)}$, where the superscript indicates that the probability is associated with expansion of $b_f(t)$ to first order:

$$\mathcal{P}_{if}^{(1)}(t) = \left| \lambda b_f^{(1)}(t) \right|^2 = \frac{\lambda^2}{\hbar^2} \left| \int_{t_0}^{t} dt' \, e^{i\omega_{fi}t'} W_{fi}(t') \right|^2$$

Pulse perturbations are perturbations for which $\lambda \hat{W} = 0$ when the system is known to be in the initial state $|\varphi_i\rangle$. The perturbation then turns on and off again, after which the probability $\mathcal{P}_{if}$ of finding the system in state $|\varphi_f\rangle$ is determined. In such cases, the temporal limits in the $\lambda b_n^{(1)}(t)$ integral can formally be extended to $-\infty$ and ∞. The integral for $\lambda b_n^{(1)}(t)$ is then

$$\lambda b_f^{(1)} = \frac{\lambda}{i\hbar} \mathcal{F}\{W_{fi}(t')\}_{\omega = -\omega_{fi}}$$

where $\mathcal{F}\{W_{fi}(t')\}_{\omega = -\omega_{fi}} = \int_{-\infty}^{\infty} dt' \, e^{i\omega_{fi}t'} W_{fi}(t')$ is the **time-domain Fourier transform** (page 94) of $W_{fi}(t')$ evaluated at frequency $\omega = -\omega_{fi}$.

For a pulse perturbation, the first-order transition probability from an initial state $|\varphi_i\rangle$ to a final state $|\varphi_f\rangle$ is

$$\mathcal{P}_{if}^{(1)} = \frac{\lambda^2}{\hbar^2} \left| \mathcal{F}\{W_{fi}(t')\}_{\omega = -\omega_{fi}} \right|^2$$

Fourier Transform Pairs for Pulse Perturbations

A time-domain function $f(t)$ has a corresponding frequency-domain function $F(\omega)$ that is the Fourier transform of $f(t)$.

The Fourier and inverse Fourier transform relationships between $f(t)$ and $F(\omega)$ are

$$F(\omega) = \mathcal{F}\{f(t)\} = \int_{-\infty}^{\infty} dt\, e^{-i\omega t} f(t)$$

$$f(t) = \mathcal{F}^{-1}\{F(\omega)\} = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega\, e^{i\omega t} F(\omega)$$

Note that these transforms are defined differently than the transforms between the position and momentum representations of a wavefunction (page 24).

Each row of the following table gives a Fourier transform pair of functions $f(t)$ and $F(\omega)$ that can be associated with pulse perturbations. Note that for all examples given, $f(t)$ is free of dimensional units and has a peak value of 1.

Fourier Transform Pairs	
$f(t)$	$F(w)$
$e^{-t^2/(2\tau^2)}$	$\tau\sqrt{2\pi}\, e^{-\omega^2\tau^2/2}$
$e^{-|t|/\tau}$	$\frac{2\tau}{1+\omega^2\tau^2}$
$\frac{1}{1+t^2/\tau^2}$	$\pi\tau e^{-|\omega|\tau/(2\pi)}$
$\mathrm{rect}(t/\tau)$	$\tau\,\mathrm{sinc}(\omega\tau/2)$
$\mathrm{rect}(t/\tau - 1/2)$	$\tau\, e^{-i\omega\tau/2}\mathrm{sinc}(\omega\tau/2)$
$\mathrm{sinc}(\pi t/\tau)$	$\tau\,\mathrm{rect}[\omega\tau/(2\pi)]$
$\Lambda(t/\tau) = \begin{cases} 1-|t|/\tau & |t|/\tau \le 1 \\ 0 & \text{otherwise} \end{cases}$	$\frac{\tau}{2}\mathrm{sinc}^2(\omega\tau/4)$

The special functions rect and sinc are defined as follows:

$$\mathrm{rect}(\xi) = \begin{cases} 1 & -\tfrac{1}{2} \le \xi \le \tfrac{1}{2} \\ 0 & \text{otherwise} \end{cases}$$

$$\mathrm{sinc}(\xi) = \frac{1}{\xi}\sin(\xi)$$

TDPT: Harmonic Perturbations

sinusoidal perturbation

The special case of harmonic perturbations involves time-dependent perturbations $\lambda\hat{W}(t) = \lambda\hat{\mathcal{W}}\sin(\omega t)$ with matrix elements $W_{fi}(t) = \mathcal{W}_{fi}\sin(\omega t)$, where $\hat{\mathcal{W}}$ is time independent. The $t = 0$ initial state is assumed to be $|\Psi(0)\rangle = |\varphi_i\rangle$, and the time and frequency-dependent transition probability $\mathcal{P}_{if}(t, \omega)$ to a final state $|\varphi_f\rangle$ is to be approximately determined.

To reach the solutions given below, the following assumptions are made:

- $|\omega|$ is sufficiently near $|\omega_{fi}|$ such that the conditions $\big||\omega_{fi}| - |\omega|\big| \ll |\omega_{fi}|$ and $\big||\omega_{fi}| - |\omega|\big| \ll |\omega|$ are satisfied. These conditions allow for a simplification in the calculation of $\mathcal{P}_{if}(t, \omega)$ that is called the **resonant approximation** or the **rotating wave approximation**.

- The duration of the perturbation is long enough that ω is well defined (i.e., there are many cycles of the harmonic perturbation during the interaction time).

- The transition probability remains small: $\mathcal{P}_{if}(t, \omega) \ll 1$ for all t and ω considered.

The last two assumptions above are together expressed as the double inequality (for $t > 0$)

$$\frac{1}{|\omega|} \ll t \ll \frac{\hbar}{|\lambda\mathcal{W}_{fi}|}$$

Within these limits and approximations, the first-order transition probability as a function of t and ω is given by

$$\mathcal{P}_{if}^{(1)}(t, \omega) = \frac{|\lambda\mathcal{W}_{fi}|^2}{4\hbar^2}\left\{\frac{\sin(t\Delta/2)}{\Delta/2}\right\}^2 = \left|\frac{\Omega_{fi}}{\Delta}\right|^2\sin^2\left(\frac{t\Delta}{2}\right)$$

where $\Delta \equiv \omega - \omega_{fi}$, and $\Omega_{fi} \equiv \lambda\mathcal{W}_{fi}/\hbar$. When $\lambda\hat{W}(t)$ primarily couples $|\varphi_i\rangle$ to $|\varphi_f\rangle$ and no other states, this result is approximately equal to the results for Rabi oscillations of a two-level system (page 76) in the limit that Δ is much larger than the resonant Rabi frequency.

Central Potential Problems

A 3D **central potential** problem consists of a particle of mass m in a spherically symmetric potential well $V(r)$, where $r = |\mathbf{r}|$, and $\mathbf{r} = (x, y, z)$. For a time-independent potential, a general central-potential Hamiltonian is written in the position representation as

$$H_{\{\mathbf{r}\}} = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$$

Because $[\hat{H}, \hat{\mathbf{L}}^2] = [\hat{H}, \hat{L}_z] = 0$ for a central potential, there exists a set of quantum states that are common eigenstates of the CSCO $\{\hat{H}, \hat{\mathbf{L}}^2, \hat{L}_z\}$. These eigenstates are often labeled with the quantum numbers n, l, and m_l, defined by the set of eigenvalue equations

$$\hat{H}|n, l, m_l\rangle = E_{n,l}|n, l, m_l\rangle$$

$$\hat{\mathbf{L}}^2|n, l, m_l\rangle = l(l+1)\hbar^2|n, l, m_l\rangle$$

$$\hat{L}_z|n, l, m_l\rangle = m_l\hbar|n, l, m_l\rangle$$

where the energy eigenvalues $E_{n,l}$ depend on a **principal quantum number** n and the OAM quantum number l, and can only be determined once $V(r)$ is specified. For any central potential, the energy eigenvalues do not depend on m_l, and l and m_l are limited to the ranges

$$\{l \in \mathbb{N}^0\}; \quad m_l \in \{-l, -l+1, \ldots, l-1, l\} \quad \text{for any } l$$

The quantum number l is further constrained by n. In the position representation, the $\{|n, l, m_l\rangle\}$ state vectors are expressed in spherical coordinates as

$$\psi_{n,l,m_l}(r, \theta, \phi) = \langle \mathbf{r}|n, l, m_l\rangle = \mathcal{R}_{n,l}(r)Y_l^{m_l}(\theta, \phi)$$

where the angular functions $Y_l^{m_l}(\theta, \phi)$ are spherical harmonics, and the radial functions $\mathcal{R}_{n,l}(r)$ can only be determined once $V(r)$ is specified. The "spinless" hydrogen problem (pages 97–98) and the 3D isotropic harmonic oscillator (page 62) are examples of central potential problems, although the energy eigenfunctions of the latter problem are usually expressed as products of Hermite–Gaussian functions (page 54) rather than as products of radial functions and spherical harmonics.

"Spinless" Hydrogen: Energy Eigenvalues

A **hydrogen** atom consists of an **electron** and **proton** bound together by the **Coulomb interaction**, given in SI units as

$$V(r) = \frac{-e^2}{4\pi\epsilon_0 r}$$

where $-e$ is the charge of an electron, ϵ_0 is the permittivity of free space (values of physical constants are given on page 125), and $r = |\mathbf{r}|$ is the coordinate for the distance between the electron and proton.

The **"spinless" hydrogen** atom problem assumes non-relativistic electron motion and that the electron and proton have zero spin. This model is an exactly solvable central potential problem and provides a good approximation to the energy eigenvalues of the "real" hydrogen atom. Once the solutions are known, better approximations can be obtained using stationary perturbation theory. In the center-of-mass frame of the atom, the spinless hydrogen problem is defined by the Hamiltonian

$$\hat{H}_0 = \frac{1}{2\mu}\hat{\mathbf{P}}^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\hat{\mathbf{R}}|}$$

The **reduced mass** μ is defined as

$$\mu = \frac{m_e\, m_p}{m_e + m_p} \approx m_e$$

where m_e and m_p are electron and proton masses (not angular momentum quantum numbers). In the position representation, where division by $|\hat{\mathbf{R}}|$ acts as division by r, the Hamiltonian is

$$H_{0_{\{r\}}} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

The eigenvalues of $\hat{H}_0$ are given by

$$E_n = -E_I/n^2; \qquad \{n \in \mathbb{N}^+\}$$

where $E_I \approx 13.6$ eV is the ground-state **ionization energy** of hydrogen, and n is the principal quantum number.

Spinless Hydrogen: Energy Eigenfunctions

The spinless hydrogen energy-eigenvalue problem is solved in the position representation using spherical coordinates. Since this is a central potential problem, the angular parts of the energy eigenfunctions are spherical harmonics $Y_l^{m_l}(\theta,\phi)$ (see page 100). The full expression for the hydrogen energy eigenfunctions (in the position representation) is

$$\psi_{n,l,m_l}(r,\theta,\phi) = \mathcal{R}_{n,l}(r)\,Y_l^{m_l}(\theta,\phi)$$

$$\{n \in \mathbb{N}^+; \quad l \in \mathbb{N}^0 \,|\, 0 \le l < n; \quad m_l \in \mathbb{Z} \,|\, -l \le m_l \le l\}$$

where $\mathcal{R}_{n,l}(r)$ are the **radial wavefunctions** for hydrogen (see page 99). The radial wavefunctions are expressed in terms of the **Bohr radius** $a_0 \equiv \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \approx 0.5 \times 10^{-10}$ m, a length constant used in atomic physics that defines an approximate radius of a ground-state hydrogen atom. The spherical harmonics and the radial wavefunctions are separately normalized, and while the spherical harmonics form an orthonormal basis for functions of θ and ϕ, the radial wavefunctions do not separately constitute an orthogonal basis set for functions of r.

The energy eigenfunctions give the wavefunction for the electron, with the proton's position defining the coordinate system origin. Each energy eigenfunction ψ_{n,l,m_l} is the position representation of the energy eigenstate $|n,l,m_l\rangle$. The energy eigenstates form an orthonormal basis $\{|n,l,m_l\rangle\}$:

$$\langle n',l',m_{l'}|n,l,m_l\rangle$$

$$= \int_0^\infty dr\, r^2 \int_0^\pi d\theta\, \sin\theta \int_0^{2\pi} d\phi\, (\psi_{n',l',m_{l'}})^*\,\psi_{n,l,m_l}$$

$$= \left(\int_0^\infty dr\, r^2 \mathcal{R}_{n',l'}\mathcal{R}_{n,l}\right)\left(\int_0^\pi d\theta\, \sin\theta \int_0^{2\pi} d\phi\, [Y_{l'}^{m_{l'}}]^*[Y_l^{m_l}]\right)$$

$$= (\delta_{n,n'})(\delta_{l,l'})(\delta_{m_l,m_{l'}})$$

> The ground state of "spinless" hydrogen is denoted $|n=1, l=0, m_l=0\rangle$, or $|1,0,0\rangle$, with energy eigenvalue $E_1 = -E_I$ and a spherically symmetric wavefunction:
>
> $$\psi_{1,0,0}(r) = \mathcal{R}_{1,0}(r)Y_0^0(\theta,\phi) = (\pi a_0^3)^{-1/2}\, e^{-r/a_0}$$
>
> Because $l=0$, the electron in the hydrogen ground state has no orbital angular momentum and therefore should not be described as "orbiting" the proton.

Hydrogen Radial Wavefunctions

The radial wavefunctions $\mathcal{R}_{n,l}(r)$ of hydrogen are given by

$$\mathcal{R}_{n,l}(r) = \left(\frac{2}{na_0}\right)^{3/2} \sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}} \left(\frac{2r}{na_0}\right)^l e^{-\frac{r}{na_0}} \mathcal{L}_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right)$$

where a_0 is the Bohr radius;

$$\mathcal{L}_{q-p}^p(u) \equiv (-1)^p \left(\frac{d}{du}\right)^p L_q(u)$$

is an **associated Laguerre polynomial**; and

$$L_q(u) \equiv e^u \left(\frac{d}{du}\right)^q (e^{-u} u^q)$$

is the qth **Laguerre polynomial**. The radial wavefunctions are not all mutually orthogonal. However, radial wavefunctions with the same quantum number l are orthogonal (note that the radial wavefunctions are all real):

$$\int_0^\infty dr\, r^2 \mathcal{R}_{n',l} \mathcal{R}_{n,l} = \delta_{n,n'}$$

Radial Wavefunctions of Hydrogen through $n = 4$
$\mathcal{R}_{1,0} = 2a_0^{-3/2} e^{-r/a_0}$
$\mathcal{R}_{2,0} = \frac{1}{\sqrt{2}} a_0^{-3/2} \left(1 - \frac{1}{2}\frac{r}{a_0}\right) e^{-r/2a_0}$
$\mathcal{R}_{2,1} = \frac{1}{\sqrt{24}} a_0^{-3/2} \left(\frac{r}{a_0}\right) e^{-r/2a_0}$
$\mathcal{R}_{3,0} = \frac{2}{\sqrt{27}} a_0^{-3/2} \left(1 - \frac{2}{3}\frac{r}{a_0} + \frac{2}{27}\left(\frac{r}{a_0}\right)^2\right) e^{-r/3a_0}$
$\mathcal{R}_{3,1} = \frac{8}{27\sqrt{6}} a_0^{-3/2} \left(1 - \frac{1}{6}\frac{r}{a_0}\right) \left(\frac{r}{a_0}\right) e^{-r/3a_0}$
$\mathcal{R}_{3,2} = \frac{4}{81\sqrt{30}} a_0^{-3/2} \left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}$
$\mathcal{R}_{4,0} = \frac{1}{4} a_0^{-3/2} \left(1 - \frac{3}{4}\frac{r}{a_0} + \frac{1}{8}\left(\frac{r}{a_0}\right)^2 - \frac{1}{192}\left(\frac{r}{a_0}\right)^3\right) e^{-r/4a_0}$
$\mathcal{R}_{4,1} = \frac{\sqrt{5}}{16\sqrt{3}} a_0^{-3/2} \left(1 - \frac{1}{4}\frac{r}{a_0} + \frac{1}{80}\left(\frac{r}{a_0}\right)^2\right) \left(\frac{r}{a_0}\right) e^{-r/4a_0}$
$\mathcal{R}_{4,2} = \frac{1}{65\sqrt{5}} a_0^{-3/2} \left(1 - \frac{1}{12}\frac{r}{a_0}\right) \left(\frac{r}{a_0}\right)^2 e^{-r/4a_0}$
$\mathcal{R}_{4,3} = \frac{1}{768\sqrt{35}} a_0^{-3/2} \left(\frac{r}{a_0}\right)^3 e^{-r/4a_0}$

Spherical Harmonics

The spherical harmonics are special functions defined on the surface of a sphere of arbitrary radius. They are denoted $Y_l^m(\theta, \phi)$ with $\{l, m \in \mathbb{N}^0 \mid -l \le m \le l\}$. Following the usual conventions of quantum physics, the spherical harmonics are given by

$$Y_l^m(\theta, \phi) = i^{\{m+|m|\}} \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} \, e^{im\phi} P_l^m(\cos\theta)$$

where

$$P_l^m(\xi) = (1 - \xi^2)^{\frac{|m|}{2}} \left(\frac{d}{d\xi}\right)^{|m|} \left\{ \frac{1}{2^l l!} \left(\frac{d}{d\xi}\right)^l (\xi^2 - 1)^l \right\}$$

is an **associated Legendre polynomial**. The quantity in curly brackets is the **Legendre polynomial** $P_l(\xi)$. The spherical harmonics form a basis for functions of θ and ϕ. Their orthonormality is expressed as

$$\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi [Y_{l'}^{m'}]^* [Y_l^m] = (\delta_{l,l'})(\delta_{m,m'})$$

Spherical Harmonics through $l = 3$
$Y_0^0 = \sqrt{\frac{1}{4\pi}}$
$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta$
$Y_1^{\pm 1} = \mp\sqrt{\frac{3}{8\pi}} \sin\theta \, e^{\pm i\phi}$
$Y_2^0 = \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1)$
$Y_2^{\pm 1} = \mp\sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta \, e^{\pm i\phi}$
$Y_2^{\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^2\theta \, e^{\pm 2i\phi}$
$Y_3^0 = \sqrt{\frac{7}{16\pi}} (5\cos^3\theta - 3\cos\theta)$
$Y_3^{\pm 1} = \mp\sqrt{\frac{21}{64\pi}} \sin\theta(5\cos^2\theta - 1)e^{\pm i\phi}$
$Y_3^{\pm 2} = \sqrt{\frac{105}{32\pi}} \sin^2\theta \cos\theta \, e^{\pm 2i\phi}$
$Y_3^{\pm 3} = \mp\sqrt{\frac{35}{64\pi}} \sin^3\theta \, e^{\pm 3i\phi}$

Atomic Angular Momentum Quantum Numbers

Various types of angular momenta associated with atoms are listed in the table below, represented by a letter that is conventionally used as the quantum number associated with the magnitude of the angular momentum. The symbol for the associated *z*-component magnetic quantum number in all cases is *m* with the given angular momentum quantum number as a subscript. For example, since *I* is the quantum number for the magnitude of nuclear spin, m_I is the *z*-component magnetic quantum number for the nuclear spin.

The standard symbol for an angular momentum quantum number is often the same as the standard symbol for the angular momentum operator, so the meaning of a symbol must often be determined by the context in which it is used. In this *Field Guide*, operators are always indicated with carets (or "hats") over the symbols to aid in the interpretation of expressions. Vector notation and subscripts further help identify the meaning of a symbol. Note that operators are not necessarily denoted with carets in other books and resources.

Quantum Number	Angular Momentum (AM) Type
l	orbital AM of a single electron
s	spin AM of a single electron
L	net orbital AM of all electrons in an atom
S	net spin AM of all electrons in an atom
J	net orbital + spin AM of all electrons in an atom; vector AM operator: $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$
I	spin AM of an atomic nucleus
F	total atomic AM; vector AM operator: $\hat{\mathbf{F}} = \hat{\mathbf{J}} + \hat{\mathbf{I}}$

L26   Fine Structure of Hydrogen: Perturbation Terms

The spinless hydrogen model (page 97) neglects physical effects arising from the electron's spin, relativistic motion, and small-scale rapid position oscillations (called **zitterbewegung**) that require the evaluation of the Coulomb potential over a spatial volume. When the dominant terms associated with these corrections are included in the hydrogen problem, the energy levels from the spinless hydrogen model are found to shift and to split; this energy-level structure is called the **fine structure** of hydrogen. When the nuclear spin is also considered, an even finer splitting of the energy levels is found; this is the **hyperfine structure** of hydrogen.

The fine-structure problem is exactly solvable using the **Dirac equation**, which is beyond the scope of this *Field Guide*, or approximately solved using stationary perturbation theory. In the latter approach, discussed below, the small expansion parameter is α^2, where α is the dimensionless **fine-structure constant**:

$$\alpha \equiv \frac{1}{4\pi\epsilon_0}\frac{e^2}{\hbar c} = \frac{\hbar}{m_e c a_0} \sim 1/137$$

where the constants are defined on page 125. The unperturbed Hamiltonian is given by the spinless hydrogen Hamiltonian $\hat{H}_0$ (page 97) with the eigenvalues $E_n = -E_I/n^2$ and eigenstates $\{|n, l, m_l\rangle\}$. The electron spin states $\{|s = 1/2, m_s = \pm 1/2\rangle\}$ are incorporated using a tensor-product basis often denoted as either $\{|n, l, m_l\rangle|s, m_s\rangle\}$ or $\{|n, l, s; m_l, m_s\rangle\}$.

The fine-structure Hamiltonian is $\hat{H}_{FS} = \hat{H}_0 + \hat{W}_{FS}$. The components of the perturbation $\hat{W}_{FS} = \alpha^2 \hat{W}_{SO} + \alpha^2 \hat{W}_R + \alpha^2 \hat{W}_D$ are defined as

$$L \cdot S = (1/2)(J^2 - L^2 - S^2).$$

- **Spin–orbit coupling:** $\alpha^2 \hat{W}_{SO} = \alpha^2 \cdot \frac{a_0^2}{2\hbar^2 \hat{R}}\frac{dV(\hat{R})}{d\hat{R}}\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$
- **Relativistic term:** $\alpha^2 \hat{W}_R = -\alpha^2 \cdot \frac{a_0^2}{8m_e\hbar^2}\hat{\mathbf{P}}^4$
- **"Darwin" term:** $\alpha^2 \hat{W}_D = \alpha^2 \cdot \frac{1}{8}a_0^2 \nabla^2 V(\hat{R}) = \alpha^2 \cdot \frac{a_0^2 e^2}{8\epsilon_0}\delta(\hat{\mathbf{R}})$

where $\hat{\mathbf{P}}^4 = (\hat{\mathbf{P}} \cdot \hat{\mathbf{P}})^2$, $\hat{R} \equiv |\hat{\mathbf{R}}|$, $V(\hat{R})$ is the Coulomb interaction energy, $\hat{\mathbf{L}}$ is the electron OAM operator, and $\hat{\mathbf{S}}$ is the $s = 1/2$ electron spin operator.

Fine Structure of Hydrogen: Solutions

The fine-structure perturbations break some of the degeneracies of the $\{|n, l, s; m_l, m_s\rangle\}$ states. Under the perturbation, the eigenstates of $\hat{H}_{FS}$ remain eigenstates of $\hat{\mathbf{L}}^2$ and $\hat{\mathbf{S}}^2$. They are also eigenstates of $\hat{\mathbf{J}}^2$ and $\hat{J}_z$ where $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$, so they are therefore not eigenstates of $\hat{L}_z$ and $\hat{S}_z$. Due to this, the eigenstates of $\hat{H}_{FS}$ involve new quantum numbers J and m_J (associated with $\hat{\mathbf{J}}^2$ and $\hat{J}_z$, respectively) instead of m_l and m_s.

The notation used below involves the standard symbols for atomic angular momentum quantum numbers (page 101). Note that it is common to use capital letters L and S as the quantum numbers for the total orbital angular momentum and the total spin of all electrons in an atom, respectively. In hydrogen, with one electron, L is equivalent to l, and S is equivalent to s. The eigenstates of $\hat{H}_{FS}$ can therefore be labeled $|n, L, S; J, m_J\rangle$. Transformations between the $\{|n, L, S; J, m_J\rangle\}$ basis and the $\{|n, L, S; m_L, m_S\rangle\}$ basis are accomplished through the use of Clebsch–Gordan coefficients.

The quantum numbers J and m_J are defined through the eigenvalue equations

$$\hat{\mathbf{J}}^2|n, L, S; J, m_J\rangle = J(J+1)\hbar^2|n, L, S; J, m_J\rangle$$

$$\hat{J}_z|n, L, S; J, m_J\rangle = m_J\hbar|n, L, S; J, m_J\rangle$$

For arbitrary L and S, J can be any value in the range $\{|L - S|, |L - S| + 1, \ldots, L + S - 1, L + S\}$. Since $S = 1/2$ for hydrogen, J can be either $L + 1/2$ or $L - 1/2$ for $L > 0$. If $L = 0$, then $J = 1/2$. For each J: $m_J \in \{-J, -J + 1, \ldots, J - 1, J\}$.

Stationary perturbation theory to first order in α^2 gives the following approximate energy eigenvalues for the hydrogen fine-structure problem:

$$E_{n,J} = E_n\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{J + 1/2} - \frac{3}{4}\right)\right]$$

L26

Hyperfine Structure of Hydrogen

The hydrogen nucleus is a single proton, so the nucleus has a spin quantum number $I = 1/2$. The nuclear spin and electronic state spaces are merged to give a tensor-product basis $\{|n, L, S; J, m_J\rangle|I, m_I\rangle\}$. These are not eigenstates of the full atomic Hamiltonian due to coupling of the magnetic dipole moment of the proton with the electron's magnetic dipole moment. This coupling leads to the hyperfine structure of hydrogen and associated shifts in the energy eigenvalues of hydrogen that are even smaller than the fine-structure energy shifts.

Hydrogen's hyperfine structure is calculated using a perturbation Hamiltonian $\hat{W}_{HF}$ (not given here) that is much weaker than $\hat{W}_{FS}$; the approximate energy eigenstates of the perturbed Hamiltonian are $\{|n, L, S, J, I; F, m_F\rangle\}$. Quantum numbers F and m_F are associated with the observables $\hat{\mathbf{F}}^2$ and $\hat{F}_z$ where $\hat{\mathbf{F}} = \hat{\mathbf{J}} + \hat{\mathbf{I}}$ is the vector operator for the total angular momentum of the atom. $\hat{\mathbf{F}}^2$ and $\hat{F}_z$ have the eigenvalue equations
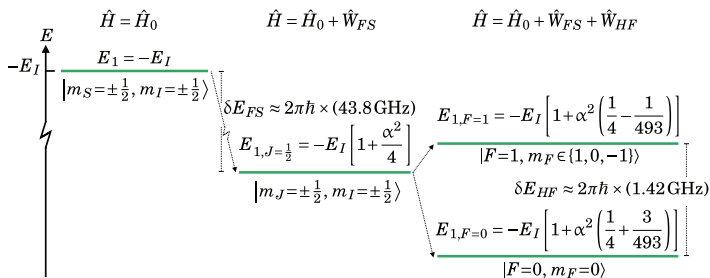
$$\hat{\mathbf{F}}^2|n, L, S, J, I; F, m_F\rangle = F(F+1)\hbar^2|n, L, S, J, I; F, m_F\rangle$$

$$\hat{F}_z|n, L, S, J, I; F, m_F\rangle = m_F\hbar|n, L, S, J, I; F, m_F\rangle$$

$$F \in \{|J-I|, |J-I|+1, \ldots, J+I-1, J+I\}$$

$$m_F \in \{-F, -F+1, \ldots, F-1, F\} \text{ for each } F$$

Since $I = 1/2$ for hydrogen, F has the values $J+1/2$ and $J-1/2$ for each J. The unperturbed, fine-structure, and hyperfine-structure energy levels, shifts, and eigenstates are shown below for the $n = 1$ level. The kets omit the quantum numbers $n = 1$, $L = 0$, $S = 1/2$, $J = 1/2$, $I = 1/2$, and $m_L = 0$.

Zeeman Effect in Hydrogen: $n = 1$

In the presence of a uniform magnetic field $\mathbf{B}$, the energy eigenvalue for the state $|n, L, S, J, I; F, m_F\rangle$ is shifted by an amount that depends on the angular momentum quantum numbers; this energy shift is the **Zeeman effect**. Let the direction of the magnetic field define the $\hat{\mathbf{z}}$ direction, so that $\mathbf{B} = B_0\hat{\mathbf{z}}$ leads to a perturbation Hamiltonian

$$\hat{W}_Z = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B}$$

with

$$\hat{\boldsymbol{\mu}} = \frac{\mu_B}{\hbar}\left(-g_L\hat{\mathbf{L}} + g_e\hat{\mathbf{S}} + g_p\frac{m_e}{m_p}\hat{\mathbf{I}}\right)$$

where $g_L \approx 1$, $g_e \approx -2.002$, and $g_p \approx 5.586$ (see page 72).

For $n = 1$, the electron has no orbital angular momentum, so the $\hat{\mathbf{L}}$ term can be neglected, and $\hat{\mathbf{S}} = \hat{\mathbf{J}}$ for this case. Since $m_e \ll m_p$, the atomic magnetic moment is approximately

$$\hat{\boldsymbol{\mu}} \approx \frac{2\mu_B}{\hbar}\hat{\mathbf{S}} = \frac{2\mu_B}{\hbar}\hat{\mathbf{J}}$$

Defining $\omega_0 \equiv \mu_B B_0/\hbar$, the Zeeman perturbation (for $n = 1$) is

$$\hat{W}_Z \approx 2\omega_0\hat{J}_z$$

The hydrogen Hamiltonian is then

$$\hat{H} = \hat{H}_0 + \hat{W}_{FS} + \hat{W}_{HF} + \hat{W}_Z$$
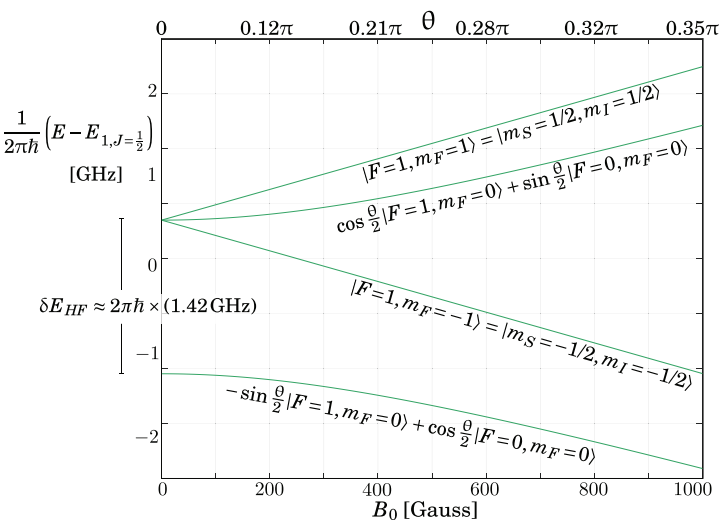
For weak magnetic fields, $\hat{W}_Z \ll \hat{W}_{HF}$, and the Zeeman effect is treated as a small perturbation to the hyperfine structure of hydrogen. This leads to the **weak-field Zeeman effect**. For larger magnetic fields, with $\hat{W}_{HF} \ll \hat{W}_Z \ll \hat{W}_{FS}$, the Zeeman effect shifts the fine-structure energy levels according to the value of m_J; the hyperfine term $\hat{W}_{HF}$ is then treated as a small perturbation on the levels $|n, L, S, J, I; m_J, m_I\rangle$ that are shifted in energy by the magnetic field. This is the **strong-field Zeeman effect**. The energy eigenvalues within both limits, as well as the **intermediate-field Zeeman effect**, can be found using stationary perturbation theory; results for the $n = 1$ level are given and illustrated on page 106.

Zeeman Effect in Hydrogen: $n = 1$ Solutions

The approximate energy eigenvalues and eigenstates for the $n = 1$ level of hydrogen in the presence of a uniform magnetic field $\mathbf{B} = B_0\hat{\mathbf{z}}$ are given and plotted below in terms of the $n = 1$ level's hyperfine splitting δE_{HF} (defined in the figure on page 104), $\omega_0 \equiv \mu_B B_0/\hbar$, and $\theta \equiv \tan^{-1}(2\hbar\omega_0/\delta E_{HF})$.

For all of the $n = 1$ states, $L = 0$, $S = 1/2$, $J = 1/2$, and $I = 1/2$; these labels are omitted from the kets given below. Furthermore, m_s is used instead of m_J since $m_L = 0$ for this case.

Energy Eigenvalues	Energy Eigenstates
$\frac{\delta E_{HF}}{4} + \hbar\omega_0$	$\lvert F = 1, m_F = 1\rangle$
$-\frac{\delta E_{HF}}{4} + \sqrt{\left(\frac{\delta E_{HF}}{2}\right)^2 + (\hbar\omega_0)^2}$	$\cos\frac{\theta}{2}\lvert F = 1, m_F = 0\rangle$ $+ \sin\frac{\theta}{2}\lvert F = 0, m_F = 0\rangle$
$\frac{\delta E_{HF}}{4} - \hbar\omega_0$	$\lvert F = 1, m_F = -1\rangle$
$-\frac{\delta E_{HF}}{4} - \sqrt{\left(\frac{\delta E_{HF}}{2}\right)^2 + (\hbar\omega_0)^2}$	$-\sin\frac{\theta}{2}\lvert F = 1, m_F = 0\rangle$ $+ \cos\frac{\theta}{2}\lvert F = 0, m_F = 0\rangle$

Spectroscopic Notation and Term Symbols

Spectroscopic notation is used to indicate the value of the OAM quantum number of a single electron within an atom. The lowest few values of l are assigned the following letters:

$$l = 0 \quad \leftrightarrow \quad s$$
$$l = 1 \quad \leftrightarrow \quad p$$
$$l = 2 \quad \leftrightarrow \quad d$$
$$l = 3 \quad \leftrightarrow \quad f$$
$$l = 4 \quad \leftrightarrow \quad g$$

These letters are used immediately following the principal quantum number n to identify an energy level. For example, the $4p$ level of hydrogen denotes $n = 4$ and $l = 1$. The $4p$ level consists of the set of three $|n, l, m_l\rangle$ states $|4, 1, 1\rangle$, $|4, 1, 0\rangle$, and $|4, 1, -1\rangle$.

When OAM quantum numbers are associated with the net OAM of all electrons in an atom (i.e., L instead of l), the same spectroscopic notation is used but the letters are capitalized. In either case, symbols must be interpreted in context, as various meanings are assigned to these letters throughout quantum and atomic physics.

The angular momentum quantum numbers S, L, and J for all electrons of an atom can also be incorporated into an atomic **term symbol**, following the notation

$$^{2S+1}L_J$$

where the superscript $2S+1$ is the **spin multiplicity** (the number of orthogonal spin states for total electron spin quantum number S), L is the total electron OAM quantum number and is replaced by the equivalent (capitalized) letter given by the spectroscopic notation convention, and J is the quantum number associated with the sum of the net electron spin and OAM for a given level. For example, all states of hydrogen have $S = 1/2$, so the spin multiplicity is 2. For a hydrogen atom in a state that has $L = 1$ and $J = 3/2$, the term symbol is $^2P_{3/2}$, and the possible values of m_J associated with this level are $3/2$, $1/2$, $-1/2$, and $-3/2$.

Identical Particles: Two Particles

A spin quantum number is associated with every quantum-mechanical particle, whether the particle is elementary (such as an electron), composite (such as an atom), or force-mediating (such as a photon). The **many-body states** available to a system of **identical particles** each having spin s may be tentatively described as if each particle could be separately labeled and assigned an individual single-particle state. The actual quantum states physically available to a system of identical particles are then constructed, as shown below.

Consider two identical particles in states $|\psi_A\rangle$ and $|\psi_B\rangle$. At first consideration, a two-particle state might be labeled $|\psi_A\rangle|\psi_B\rangle$, where the first ket is the state of (nominal) "particle 1," and the second is that of (nominal) "particle 2." However, since the particles are identical, no measurement can distinguish this state from $|\psi_B\rangle|\psi_A\rangle$ (i.e., "particle 1" in state $|\psi_B\rangle$ and "particle 2" in state $|\psi_A\rangle$), so these two tensor product kets cannot be different elements of the state space of the two-particle system. The physically available two-particle states are rather

+ sign = bosons
- sign = fermions

$$|\Psi\rangle = \frac{\beta}{\sqrt{2}}(|\psi_A\rangle|\psi_B\rangle \pm |\psi_B\rangle|\psi_A\rangle)$$

The plus sign is used if the particles have integer (including 0) spin; these particles are called **bosons**. The minus sign is used if the particles have half-integer spin (1/2, 3/2, etc.); these particles are called **fermions**. The normalization coefficient β depends on states $|\psi_A\rangle$ and $|\psi_B\rangle$: $\beta = 1$ if $\langle\psi_A|\psi_B\rangle = 0$, but $\beta \neq 1$ otherwise and must be found after constructing the superposition so that $\langle\Psi|\Psi\rangle = 1$.

If $|\psi_A\rangle = |\psi_B\rangle$, then (after normalizing the boson case)

$$|\Psi\rangle = \begin{cases} |\psi_A\rangle|\psi_A\rangle & \text{(bosons)} \\ 0 & \text{(fermions)} \end{cases}$$

The boson state above is an element of the two-particle state space; the fermion case is not ($|\Psi\rangle = 0$ is not a physical state). The conclusion from this result is that two identical fermions cannot occupy the same single-particle quantum state; this is the **Pauli exclusion principle.** same than the one in electronic configuration

Identical Particles: Three or More Particles

Three-particle case: The physical state of three identical fermions in orthogonal single-particle quantum states $|\psi_A\rangle$, $|\psi_B\rangle$, and $|\psi_C\rangle$ is given by

$$|\Psi\rangle = \frac{1}{\sqrt{6}} \begin{vmatrix} |\psi_A\rangle & |\psi_B\rangle & |\psi_C\rangle \\ |\psi_A\rangle & |\psi_B\rangle & |\psi_C\rangle \\ |\psi_A\rangle & |\psi_B\rangle & |\psi_C\rangle \end{vmatrix}$$

$$= \frac{1}{\sqrt{6}} (|\psi_A\rangle|\psi_B\rangle|\psi_C\rangle - |\psi_A\rangle|\psi_C\rangle|\psi_B\rangle + |\psi_B\rangle|\psi_C\rangle|\psi_A\rangle$$
$$- |\psi_B\rangle|\psi_A\rangle|\psi_C\rangle + |\psi_C\rangle|\psi_A\rangle|\psi_B\rangle - |\psi_C\rangle|\psi_B\rangle|\psi_A\rangle)$$

(labels: particle 1, particle 1, particle 2; particle 2, particle 3, particle 3)

The right side of the first expression is a **Slater determinant**. It is evaluated as a matrix determinant, although a proper order must be kept when constructing each tensor product of three kets. The first row is associated with (nominal) particle 1; the elements of this row appear first in each tensor product. The second row is associated with particle 2; these kets appear second, etc. The second expression above is the evaluated determinant. Again, these expressions show that two identical fermions cannot occupy the same single-particle state.

The three-particle quantum state (prior to finding the normalization coefficient β) of identical bosons is

$$|\Psi\rangle = \frac{\beta}{\sqrt{6}} (|\psi_A\rangle|\psi_B\rangle|\psi_C\rangle + |\psi_A\rangle|\psi_C\rangle|\psi_B\rangle + |\psi_B\rangle|\psi_C\rangle|\psi_A\rangle$$
$$+ |\psi_B\rangle|\psi_A\rangle|\psi_C\rangle + |\psi_C\rangle|\psi_A\rangle|\psi_B\rangle + |\psi_C\rangle|\psi_B\rangle|\psi_A\rangle)$$

N-particle case: For N identical fermions in states $|\psi_1\rangle$ to $|\psi_N\rangle$, the N-particle state is given by the Slater determinant

$$|\Psi\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} |\psi_1\rangle & |\psi_2\rangle & \dots & |\psi_N\rangle \\ |\psi_1\rangle & |\psi_2\rangle & \dots & |\psi_N\rangle \\ \vdots & \vdots & \ddots & \vdots \\ |\psi_1\rangle & |\psi_2\rangle & \dots & |\psi_N\rangle \end{vmatrix}$$

For N identical bosons in states $|\psi_1\rangle$ to $|\psi_N\rangle$, the same sequence of tensor-product states as above is constructed, except all of the minus signs from the Slater determinant are replaced by plus signs (this is a matrix **permanent** rather than a determinant). $|\Psi\rangle$ is then normalized.

Identical Particles: Occupation Number Basis

For a system of N identical particles, the formalism given on pages 108–109 describes the physical states that are elements of the state space $\mathcal{E}_N$ of the entire many-body system. A basis for $\mathcal{E}_N$ can be constructed using a simplified notation that enables the specification of the number of particles n_k that can be found in each single-particle state of a discrete basis $\{|\psi_k\rangle\}$ that spans the state space for a single particle; n_k is called the occupation number for state $|\psi_k\rangle$.

For example, if N identical particles are confined in a 1D potential well, and if $|\psi_1\rangle$ is the single-particle ground state of the well, then $n_1 = 3$ indicates that there are three particles in the ground state (necessarily implying that the particles are bosons). Correspondingly, $N - 3$ particles must occupy excited states. The occupation-number formalism avoids the need to invoke language and terminology that artificially label the particles.

The many-particle occupation number basis for $\mathcal{E}_N$ is specified by $\{|n_1, n_2, \cdots, n_k, \cdots\rangle\}$, where n_k is the occupation number for the kth single-particle state and is found in the kth position within the many-body ket, and $N = \sum_k n_k$.

For example, the state $|0, 1, 0, 1, 0, \cdots\rangle$ (with all other occupation numbers being zero) indicates that there is one particle in the single-particle state $|\psi_2\rangle$ and one particle in the single-particle state $|\psi_4\rangle$. This is a physical state available to a system of two identical particles, either bosons or fermions. However, the superpositions of tensor-product states are different for the boson and fermion cases. For idential bosons, the occupation-number state $|0, 1, 0, 1, 0, \cdots\rangle$ coincides with the two-particle state

$$|\Psi\rangle = \frac{1}{\sqrt{2}} \left(|\psi_2\rangle|\psi_4\rangle + |\psi_4\rangle|\psi_2\rangle \right)$$

whereas for fermions it coincides with the two-particle state

$$|\Psi\rangle = \frac{1}{\sqrt{2}} \left(|\psi_2\rangle|\psi_4\rangle - |\psi_4\rangle|\psi_2\rangle \right)$$

Identical Particles: Occupation Number Basis States

The occupation number basis states $\{|n_1, n_2, \cdots, n_k, \cdots\rangle\}$ defined on page 110 have the following properties:

- The basis is orthonormal:

$$\langle n_1', n_2', \cdots, n_k', \cdots \, | n_1, n_2, \cdots, n_k, \cdots \rangle$$
$$= (\delta_{n_1, n_1'})(\delta_{n_2, n_2'})\ldots(\delta_{n_k, n_k'})\ldots$$

- For a system of N fermions, the Pauli exclusion principle constrains each occupation number to be either 0 or 1, along with the constraint $N = \sum_k n_k$

- For a system of bosons, each occupation number may be any non-negative integer, limited only by $N = \sum_k n_k$

- For the occupation number n_k, the index k may be a compound index that represents or is replaced by a set of single-particle indices. For example, consider a 3D isotropic harmonic oscillator potential of frequency ω. The energy eigenvalues for the single-particle Hamiltonian are

$$E_{n_x, n_y, n_z} = \hbar\omega(n_x + n_y + n_z + 3/2)$$

$$\{n_x, n_y, n_z \in \mathbb{N}^0\}$$

following the notation defined on page 62. The occupation-number basis states for three identical particles (bosons or fermions) in this potential may be written as

$$\{|n_{0,0,0}, n_{1,0,0}, n_{0,1,0}, n_{0,0,1}, \cdots\rangle\}$$

where the subscripts indicate the degree of excitation of each of the three orthogonal dimensions of the oscillator. If there is no energy of interaction between the three particles, then the energy of the occupation-number state $|0, 1, 1, 1, 0, \cdots\rangle$ is $3 \cdot \frac{5}{2}\hbar\omega$.

- The occupation number basis is used in problems that involve quantifying the states and dynamics of systems of **interacting particles**, and in the formalism of **second quantization**.

Spherical Coordinates

Spherical coordinates and expressions for the conversion between rectilinear and spherical coordinate systems are defined below.

Conventionally, x, y, and z indicate orthogonal spatial coordinates in a 3D rectilinear coordinate system, where

$$\mathbf{r} = (x, y, z) = x\hat{\mathbf{x}} + y\hat{\mathbf{y}} + z\hat{\mathbf{z}}$$

is a position vector. Vectors are denoted in bold. Unit (directional) vectors have a norm of 1 and are denoted with a hat or caret over a coordinate symbol, e.g., $\hat{\mathbf{x}} = (1, 0, 0)$.
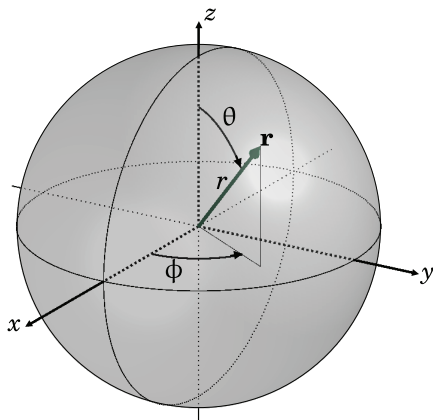
Coordinate Conversion	
$r = \lvert\mathbf{r}\rvert = \sqrt{x^2 + y^2 + z^2}$	Magnitude of $\mathbf{r}$
$\theta = \tan^{-1}\left(\frac{1}{z}\sqrt{x^2 + y^2}\right)$	Polar angle
$\phi = \tan^{-1}\left(\frac{y}{x}\right)$	Azimuthal angle
$x = r\sin\theta\cos\phi$ $y = r\sin\theta\sin\phi$ $z = r\cos\theta$	

Unit (Directional) Vector Conversion
$\hat{\mathbf{r}} = \sin\theta\cos\phi\,\hat{\mathbf{x}} + \sin\theta\sin\phi\,\hat{\mathbf{y}} + \cos\theta\,\hat{\mathbf{z}}$ $\hat{\boldsymbol{\theta}} = \cos\theta\cos\phi\,\hat{\mathbf{x}} + \cos\theta\sin\phi\,\hat{\mathbf{y}} - \sin\theta\,\hat{\mathbf{z}}$ $\hat{\boldsymbol{\phi}} = -\sin\phi\,\hat{\mathbf{x}} + \cos\phi\,\hat{\mathbf{y}}$
$\hat{\mathbf{x}} = \sin\theta\cos\phi\,\hat{\mathbf{r}} + \cos\theta\cos\phi\,\hat{\boldsymbol{\theta}} - \sin\phi\,\hat{\boldsymbol{\phi}}$ $\hat{\mathbf{y}} = \sin\theta\sin\phi\,\hat{\mathbf{r}} + \cos\theta\sin\phi\,\hat{\boldsymbol{\theta}} + \cos\phi\,\hat{\boldsymbol{\phi}}$ $\hat{\mathbf{z}} = \cos\theta\,\hat{\mathbf{r}} - \sin\theta\,\hat{\boldsymbol{\theta}}$

Operators in Spherical Coordinates

The spherical coordinates defined on page 115 are illustrated below.

The vector differential operator ∇ is given by

$$\nabla = \hat{\mathbf{r}}\frac{\partial}{\partial r} + \hat{\boldsymbol{\theta}}\frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\boldsymbol{\phi}}\frac{1}{r\sin\theta}\frac{\partial}{\partial \phi}$$

The **Laplacian** ∇^2 is given by

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial}{\partial \theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial \phi^2}$$

The 3D differential volume element $d^3\mathbf{r}$, given in Cartesian coordinates as $d^3\mathbf{r} = dx\,dy\,dz$, is expressed in spherical coordinates as

$$d^3\mathbf{r} = r^2\sin\theta\,dr\,d\theta\,d\phi$$

so that

$$\int d\phi \int d\theta \sin\theta \int dr\,r^2 f(r,\theta,\phi)$$

is an indefinite volume integral of function $f(r, \theta, \phi)$.

Clebsch–Gordan Coefficient Tables: $J_1 \times 1/2$

Tables of Clebsch–Gordan coefficients are given below and on pages 119–121. Two individual angular momentum quantum numbers are denoted J_1 and J_2, with $J_1 \geq J_2$. The corresponding z-component magnetic quantum numbers are m_1 and m_2. The columns are labeled by the total-angular-momentum quantum numbers J (magnitude) and m_J (z-component magnetic quantum number) on a green background, with J above m_J. The rows are labeled by m_1 (left) and m_2 (right) on a green background. The square-root is to be taken of every number in a table, and any minus sign (if present) is placed outside of the radical. For example, a table entry of $-4/5$ is interpreted as $-\sqrt{4/5}$. See page 88 for an example that uses Clebsch–Gordan-coefficient tables.

Notation Guide

$J_1 \times J_2$

J	J	...
m_J	m_J	...

m_1	m_2	
m_1	m_2	Coefficients
⋮	⋮	

$1/2 \times 1/2$

	1
	+1
+1/2 +1/2	1

	1	0
	0	0
+1/2 −1/2	1/2	1/2
−1/2 +1/2	1/2	−1/2

	1
	−1
−1/2 −1/2	1

$1 \times 1/2$

	3/2
	+3/2
+1 +1/2	1

	3/2	1/2
	+1/2	+1/2
+1 −1/2	1/3	2/3
0 +1/2	2/3	−1/3

	3/2	1/2
	−1/2	−1/2
0 −1/2	2/3	1/3
−1 +1/2	1/3	−2/3

	3/2
	−3/2
−1 −1/2	1

$3/2 \times 1/2$

	2
	+2
+3/2 +1/2	1

	2	1
	+1	+1
+3/2 −1/2	1/4	3/4
+1/2 +1/2	3/4	−1/4

	2	1
	0	0
+1/2 −1/2	1/2	1/2
−1/2 +1/2	1/2	−1/2

	2	1
	−1	−1
−1/2 −1/2	3/4	1/4
−3/2 +1/2	1/4	−3/4

	2
	−2
−3/2 −1/2	1

$2 \times 1/2$

	5/2
	+5/2
+2 +1/2	1

	5/2	3/2
	+3/2	+3/2
+2 −1/2	1/5	4/5
+1 +1/2	4/5	−1/5

	5/2	3/2
	+1/2	+1/2
+1 −1/2	2/5	3/5
0 +1/2	3/5	−2/5

	5/2	3/2
	−1/2	−1/2
0 −1/2	3/5	2/5
−1 +1/2	2/5	−3/5

	5/2	3/2
	−3/2	−3/2
−1 −1/2	4/5	1/5
−2 +1/2	1/5	−4/5

	5/2
	−5/2
−2 −1/2	1

Clebsch–Gordan Coefficient Tables: $J_1 \times 1$

1 × 1

		2
		+2
+1	**+1**	1

		2	**1**
		+1	**+1**
+1	**0**	1/2	1/2
0	**+1**	1/2	−1/2

		2	**1**	**0**
		0	**0**	**0**
+1	**−1**	1/6	1/2	1/3
0	**0**	2/3	0	−1/3
−1	**+1**	1/6	−1/2	1/3

		2	**1**
		−1	**−1**
0	**−1**	1/2	1/2
−1	**0**	1/2	−1/2

		2
		−2
−1	**−1**	1

3/2 × 1

		5/2
		+5/2
+3/2	**+1**	1

		5/2	**3/2**
		+3/2	**+3/2**
+3/2	**0**	2/5	3/5
+1/2	**+1**	3/5	−2/5

		5/2	**3/2**	**1/2**
		+1/2	**+1/2**	**+1/2**
+3/2	**−1**	1/10	2/5	1/2
+1/2	**0**	3/5	1/15	−1/3
−1/2	**+1**	3/10	−8/15	1/6

		5/2	**3/2**	**1/2**
		−1/2	**−1/2**	**−1/2**
+1/2	**−1**	3/10	8/15	1/6
−1/2	**0**	3/5	−1/15	−1/3
−3/2	**+1**	1/10	−2/5	1/2

		5/2	**3/2**
		−3/2	**−3/2**
−1/2	**−1**	3/5	2/5
−3/2	**0**	2/5	−3/5

		5/2
		−5/2
−3/2	**−1**	1

2 × 1

		3
		+3
+2	**+1**	1

		3	**2**
		+2	**+2**
+2	**0**	1/3	2/3
+1	**+1**	2/3	−1/3

		3	**2**	**1**
		+1	**+1**	**+1**
+2	**−1**	1/15	1/3	3/5
+1	**0**	8/15	1/6	−3/10
0	**+1**	2/5	−1/2	1/10

		3	**2**	**1**
		0	**0**	**0**
+1	**−1**	1/5	1/2	3/10
0	**0**	3/5	0	−2/5
−1	**+1**	1/5	−1/2	3/10

		3	**2**	**1**
		−1	**−1**	**−1**
0	**−1**	2/5	1/2	1/10
−1	**0**	8/15	−1/6	−3/10
−2	**+1**	1/15	−1/3	3/5

		3	**2**
		−2	**−2**
−1	**−1**	2/3	1/3
−2	**0**	1/3	−2/3

		3
		−3
−2	**−1**	1

Clebsch–Gordan Coefficient Tables: $J_1 \times 3/2$

3/2 × 3/2

		3
		+3
+3/2	**+3/2**	1

		3	2
		+2	**+2**
+3/2	**+1/2**	1/2	1/2
+1/2	**+3/2**	1/2	−1/2

		3	2	1
		+1	**+1**	**+1**
+3/2	**−1/2**	1/5	1/2	3/10
+1/2	**+1/2**	3/5	0	−2/5
−1/2	**+3/2**	1/5	−1/2	3/10

		3	2	1	0
		0	**0**	**0**	**0**
+3/2	**−3/2**	1/20	1/4	9/20	1/4
+1/2	**−1/2**	9/20	1/4	−1/20	−1/4
−1/2	**+1/2**	9/20	−1/4	−1/20	1/4
−3/2	**+3/2**	1/20	−1/4	9/20	−1/4

		3	2	1
		−1	**−1**	**−1**
+1/2	**−3/2**	1/5	1/2	3/10
−1/2	**−1/2**	3/5	0	−2/5
−3/2	**+1/2**	1/5	−1/2	3/10

		3	2
		−2	**−2**
−1/2	**−3/2**	1/2	1/2
−3/2	**−1/2**	1/2	−1/2

		3
		−3
−3/2	**−3/2**	1

2 × 3/2

		7/2
		+7/2
+2	**+3/2**	1

		7/2	5/2
		+5/2	**+5/2**
+2	**+1/2**	3/7	4/7
+1	**+3/2**	4/7	−3/7

		7/2	5/2	3/2
		+3/2	**+3/2**	**+3/2**
+2	**−1/2**	1/7	16/35	2/5
+1	**+1/2**	4/7	1/35	−2/5
0	**+3/2**	2/7	−18/35	1/5

		7/2	5/2	3/2	1/2
		+1/2	**+1/2**	**+1/2**	**+1/2**
+2	**−3/2**	1/35	6/35	2/5	2/5
+1	**−1/2**	12/35	5/14	0	−3/10
0	**+1/2**	18/35	−3/35	−1/5	1/5
−1	**+3/2**	4/35	−27/70	2/5	−1/10

		7/2	5/2	3/2	1/2
		−1/2	**−1/2**	**−1/2**	**−1/2**
+1	**−3/2**	4/35	27/70	2/5	1/10
0	**−1/2**	18/35	3/35	−1/5	−1/5
−1	**+1/2**	12/35	−5/14	0	3/10
−2	**+3/2**	1/35	−6/35	2/5	−2/5

		7/2	5/2	3/2
		−3/2	**−3/2**	**−3/2**
0	**−3/2**	2/7	18/35	1/5
−1	**−1/2**	4/7	−1/35	−2/5
−2	**+1/2**	1/7	−16/35	2/5

		7/2	5/2
		−5/2	**−5/2**
−1	**−3/2**	4/7	3/7
−2	**−1/2**	3/7	−4/7

		7/2
		−7/2
−2	**−3/2**	1

Clebsch–Gordan Coefficient Tables: 2×2

2 × 2

		4
		4
+2	+2	1

		4	3
		+3	+3
+2	+1	1/2	1/2
+1	+2	1/2	−1/2

		4	3	2
		+2	+2	+2
+2	0	3/14	1/2	2/7
+1	+1	4/7	0	−3/7
0	+2	3/14	−1/2	2/7

		4	3	2	1
		+1	+1	+1	+1
+2	−1	1/14	3/10	3/7	1/5
+1	0	3/7	1/5	−1/14	−3/10
0	+1	3/7	−1/5	−1/14	3/10
−2	+2	1/14	−3/10	3/7	−1/5

		4	3	2	1	0
		0	0	0	0	0
+2	−2	1/70	1/10	2/7	2/5	1/5
+1	−1	8/35	2/5	1/14	−1/10	−1/5
0	0	18/35	0	−2/7	0	1/5
−1	+1	8/35	−2/5	1/14	1/10	−1/5
−2	+2	1/70	−1/10	2/7	−2/5	1/5

		4	3	2	1
		−1	−1	−1	−1
+1	−2	1/14	3/10	3/7	1/5
0	−1	3/7	1/5	−1/14	−3/10
−1	0	3/7	−1/5	−1/14	3/10
−2	+1	1/14	−3/10	3/7	−1/5

		4	3	2
		−2	−2	−2
0	−2	3/14	1/2	2/7
−1	−1	4/7	0	−3/7
−2	0	3/14	−1/2	2/7

		4	3
		−3	−3
−1	−2	1/2	1/2
−2	−1	1/2	−1/2

		4
		−4
−2	−2	1