

## Appendix A

### Some Atomic Constants

Quantity	Symbol	Value in SI (cgs) units <sup>a</sup>
Speed of light in vacuum	$c$	$2.99792458 \times 10^8$ m/s ( $10^{10}$ cm/s)
Elementary charge	$e$	$1.6021765 \times 10^{-19}$ C ( $4.803242 \times 10^{-10}$ esu)
Planck's constant	$h$	$6.626069 \times 10^{-34}$ J s ( $\times 10^{-27}$ erg s)
	$\hbar$	$1.0545716 \times 10^{-34}$ J s ( $\times 10^{-27}$ erg s)
Electron rest mass	$m_e$	$9.109382 \times 10^{-31}$ kg ( $\times 10^{-28}$ g)
Boltzmann constant	$k_B$	$1.380650 \times 10^{-23}$ J/K ( $\times 10^{-16}$ erg/K)
	$k_B/hc$	( $0.6950356$ cm <sup>-1</sup> K <sup>-1</sup> )
Rydberg constant	$R_\infty$	$1.09737315685 \times 10^7$ m <sup>-1</sup> ( $\times 10^5$ cm <sup>-1</sup> )
	$R_\infty hc$	$2.179872 \times 10^{-18}$ J = 13.605691 eV
Fine-structure constant	$\alpha^{-1}$	137.0359997
Bohr radius	$a_0$	$0.529177208 \times 10^{-10}$ m ( $\times 10^{-8}$ cm)
Atomic mass unit	$1 \text{ u} = m_u$	$1.6605388 \times 10^{-27}$ kg ( $\times 10^{-24}$ g)
Proton rest mass	$m_p$	$1.6726216 \times 10^{-27}$ kg ( $\times 10^{-24}$ gm)
	$m_p/m_e$	1836.152672
Electron $g$ factor	$g_e$	-2.002319304362
Bohr magneton	$\mu_B$	$9.274009 \times 10^{-24}$ J T <sup>-1</sup>
	$\mu_B/hc$	( $4.668645 \times 10^{-5}$ cm <sup>-1</sup> gauss <sup>-1</sup> )
Nuclear magneton	$\mu_N$	$5.0507832 \times 10^{-27}$ J T <sup>-1</sup>

<sup>a</sup>P.J. Mohr, B.N. Taylor and D.B. Newell, Rev. Mod. Phys. **80**, 633 (2008)

# Appendix B

## Polynomials and Spherical Harmonics

The associated Laguerre polynomials are defined as

$$L_{\lambda}^{\mu}(x) = \frac{1}{\lambda!} x^{-\mu} e^x \frac{d^{\lambda}}{dx^{\lambda}} (x^{\lambda+\mu} e^{-x})$$

The Legendre polynomials are defined as

$$P_{\ell} = \frac{1}{2^{\ell} \ell!} \frac{d^{\ell}}{dx^{\ell}} (x^2 - 1)^{\ell}; \quad P_{\ell}(1) = 1 \quad \text{for all } \ell$$

The spherical harmonics are

$$Y_{\ell}^m(\theta, \phi) = (-1)^m e^{im\phi} \left[ \frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!} \right]^{1/2} \sin^m \theta \frac{d^m}{dx^m} P_{\ell}(x) \quad \text{for } x = \cos \theta$$

Orthonormality and completeness are given by

$$\int_0^{2\pi} \int_0^{\pi} Y_{\ell}^m(\theta, \phi) Y_{\ell'}^{*m}(\theta, \phi) \sin \theta \, d\theta \, d\phi = \delta_{\ell\ell'} \delta_{mm'} \quad (\text{B.1})$$

$$\sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} Y_{\ell}^{*m}(\theta', \phi') Y_{\ell}^m(\theta, \phi) = \delta(\phi - \phi') \delta(\cos \theta - \cos \theta') \quad (\text{B.2})$$

$$Y_\ell^{*m}(\theta, \phi) = (-1)^m Y_\ell^{-m}(\theta, \phi) \quad (\text{B.3})$$

$$Y_\ell^m(\pi - \theta, \phi + \pi) = (-1)^\ell Y_\ell^m(\theta, \phi) \quad \text{Inversion: } \vec{r} \rightarrow -\vec{r} \quad (\text{B.4})$$

$$Y_\ell^0(\theta, \phi) = \left( \frac{2\ell + 1}{4\pi} \right)^{1/2} P_\ell(\cos \theta) \quad \text{No } \phi \text{ dependence} \quad (\text{B.5})$$

$$Y_\ell^m(0, \phi) = Y_\ell^0(0) \delta_{m0} = \sqrt{\frac{2\ell + 1}{4\pi}} \delta_{m0} \quad (\text{B.6})$$

The expansion of  $\frac{1}{r_{12}}$  occurs often in this text, and its derivation will be given here:

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{4\pi}{(2\ell + 1)} \frac{r_{<}^\ell}{r_{>^{\ell+1}} Y_\ell^{*m}(\theta_2, \phi_2) Y_\ell^m(\theta_1, \phi_1) \quad (\text{B.7})$$

$\vec{r}_1$  and  $\vec{r}_2$  are arbitrary vectors having the usual spherical coordinate angles  $\theta_1, \phi_1$  and  $\theta_2, \phi_2$ , respectively. Let  $\gamma$  be the angle between these vectors,  $\hat{r}_1 \cdot \hat{r}_2 = \cos \gamma$ , such that if the  $z$ -axis of a coordinate system were aligned with either  $\vec{r}_1$  or  $\vec{r}_2$ ,  $\gamma$  would play the role of  $\theta$  for that coordinate frame. In that coordinate frame the role of  $\phi$  is played by  $\omega$ . The first step is to recall that

$$\nabla^2(|\vec{r}_1 - \vec{r}_2|^{-1}) = 0 \quad \text{except at } \vec{r}_1 = \vec{r}_2$$

If  $\vec{r}_2$  is chosen to lie along the  $z$ -axis, there is azimuthal symmetry with the solution

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \sum_{\ell=0}^{\infty} [A_\ell r^\ell + B_\ell r^{-(\ell+1)}] P_\ell(\cos \theta)$$

This is the general solution to Laplace's equation in spherical coordinates with azimuthal symmetry. Since this solution is valid everywhere (except at  $\vec{r}_1 = \vec{r}_2$ ), it must be valid for  $\vec{r}_1$  on the  $z$ -axis. Then

$$\text{RHS} = \sum_{\ell=0}^{\infty} [A_\ell r^\ell + B_\ell r^{-(\ell+1)}]$$

$$\begin{aligned} \text{LHS} &= \frac{1}{(r_1 - r_2)} = \frac{1}{r_1} (1 - r_2/r_1)^{-1} \quad r_1 > r_2 \\ &= \frac{1}{r_1} \left[ 1 + \frac{r_2}{r_1} + \left( \frac{r_2}{r_1} \right)^2 + \left( \frac{r_2}{r_1} \right)^3 + \cdots \right] \\ &= \frac{1}{r_1} \sum_{\ell=0}^{\infty} \left( \frac{r_2}{r_1} \right)^\ell = \sum_{\ell=0}^{\infty} \frac{r_2^\ell}{r_1^{\ell+1}} \end{aligned}$$

which holds whenever  $r_1 > r_2$ . Whenever  $r_2 > r_1$ , one obtains

$$\text{LHS} = \sum_{\ell=0}^{\infty} \frac{r_1^\ell}{r_2^{\ell+1}}$$

These two possibilities can be combined into the single expression:

$$\text{LHS} = \sum_{\ell=0}^{\infty} \frac{r_{<}^\ell}{r_{>}^{\ell+1}}$$

where  $r_{<}$  ( $r_{>}$ ) is the lesser (greater) of  $r_1$  and  $r_2$ . This is compatible with the right-hand side. For example, if  $r_1 > r_2$   $B_\ell = r_2^\ell$  and  $A_\ell = 0$  while if  $r_2 > r_1$   $A_\ell = 1/r_2^{(\ell+1)}$  and  $B_\ell = 0$ . When  $r_1$  is not along the z-axis, the solution would look like

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \sum_{\ell=0}^{\infty} \frac{r_{<}^\ell}{r_{>}^{\ell+1}} P_\ell(\cos \theta)$$

Finally if  $r_2$  had not been along the z-axis,  $\theta$  would have been  $\gamma$  yielding

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \sum_{\ell=0}^{\infty} \frac{r_{<}^\ell}{r_{>}^{\ell+1}} P_\ell(\cos \gamma). \tag{B.8}$$

It remains to show that  $P_\ell(\cos \gamma)$  can be expanded in spherical harmonics. The expression is referred to as the spherical harmonic addition theorem:

$$P_\ell(\cos \gamma) = \left( \frac{4\pi}{2\ell + 1} \right) \sum_{m=-\ell}^{\ell} Y_\ell^{*m}(\theta_2, \phi_2) Y_\ell^m(\theta_1, \phi_1) \tag{B.9}$$

First consider a function  $g(\theta, \phi)$  which will at first be identified with the spherical harmonic having coordinates  $\theta_1, \phi_1$ . It will then be expanded in spherical harmonics using  $\gamma, \omega$  coordinates. It's value at  $\gamma = 0$  will prove to be important, but at that value for  $\gamma$ , it becomes equal to the spherical harmonic having coordinates  $\theta_2, \phi_2$ . Let's see how this unfolds:

$$g(\theta_1, \phi_1) \equiv Y_\ell^m(\theta_1, \phi_1) \tag{B.10}$$

$$= \sum_{m'=-\ell}^{\ell} a_{\ell m'} Y_\ell^{m'}(\gamma, \omega) \tag{B.11}$$

No summation over  $\ell$  is needed as the spherical harmonics do not change  $\ell$  value under a coordinate rotation:

$$g(\theta_1, \phi_1)|_{\gamma=0} = \sum_{m'=-\ell}^{\ell} a_{\ell m'} \left[ \frac{(2\ell + 1)}{4\pi} \right]^{1/2} \delta_{m'0} = a_{\ell 0} \left[ \frac{(2\ell + 1)}{4\pi} \right]^{1/2} \tag{B.12}$$

This follows from property (B.6) of spherical harmonics. Using (B.11), one can see that

$$\int g(\theta_1, \phi_1) Y_\ell^{*0}(\gamma, \omega) d\Omega_{\gamma, \omega} = a_{\ell 0}$$

But from (B.10), this means that

$$\int Y_\ell^m(\theta_1, \phi_1) Y_\ell^{*0}(\gamma, \omega) d\Omega_{\gamma, \omega} = a_{\ell 0} \quad (\text{B.13})$$

It is now possible to expand  $P_\ell(\cos \gamma)$  itself in spherical harmonics:

$$P_\ell(\cos \gamma) = \sum_{m'=-\ell}^{\ell} b_{\ell m'} Y_\ell^{m'}(\theta_1, \phi_1) \quad (\text{B.14})$$

If one now multiplies both sides by  $Y_\ell^{*m}$  and integrates over all space,

$$\int P_\ell(\cos \gamma) Y_\ell^{*m} d\Omega = \sum_{m'=-\ell}^{\ell} b_{\ell m'} \delta_{mm'} = b_{\ell m} \quad (\text{B.15})$$

From Equation (B.5), it follows that

$$P_\ell(\cos \gamma) = \left[ \frac{4\pi}{(2\ell + 1)} \right]^{1/2} Y_\ell^0(\gamma, \omega)$$

though in this expression  $\omega$  is irrelevant. Inserting this into (B.15) yields

$$\left[ \frac{4\pi}{(2\ell + 1)} \right]^{1/2} \int Y_\ell^0(\gamma, \omega) Y_\ell^{*m}(\theta_1, \phi_1) d\Omega = b_{\ell m}$$

But from (B.13), it follows that

$$b_{\ell m}^* = a_{\ell 0} \left[ \frac{4\pi}{(2\ell + 1)} \right]^{1/2}$$

Substituting the right-hand side of the above from (B.12) yields

$$b_{\ell m}^* = \frac{4\pi}{(2\ell + 1)} g(\theta_1, \phi_1) |_{\gamma=0}$$

But as stated in the introduction of this derivation at  $\gamma = 0$ , one can write

$$g(\theta_1, \phi_1) |_{\gamma=0} = Y_\ell^m(\theta_2, \phi_2)$$

from which it follows that

$$b_{\ell m}^* = \frac{4\pi}{(2\ell + 1)} Y_\ell^m(\theta_2, \phi_2).$$

Taking the complex conjugate and putting back into Eq. (B.14) yields the result

$$P_\ell(\cos \gamma) = \left( \frac{4\pi}{2\ell + 1} \right) \sum_{m=-\ell}^{\ell} Y_\ell^{*m}(\theta_2, \phi_2) Y_\ell^m(\theta_1, \phi_1)$$

where the dummy index  $m'$  has been replaced by  $m$  everywhere. This completes the derivation of Equation (B.7).

Sometimes one sees spherical harmonics redefined to emphasize their relations to the Cartesian coordinates  $x$ ,  $y$ , and  $z$ . Define

$$C_\ell^m \equiv \left( \frac{2\ell + 1}{4\pi} \right)^{1/2} Y_\ell^m(\theta, \phi)$$

(eliminates some annoying constants.) Note that  $C_1^0 = \cos \theta = Z/r$ :

$$\frac{C_1^{-1} - C_1^1}{\sqrt{2}} = \sin \theta \cos \phi = x/r$$

$$\frac{C_1^{-1} + C_1^1}{-\sqrt{2}i} = \sin \theta \sin \phi = y/r$$

These linear combinations have the spatial symmetries of  $x$ ,  $y$ , and  $z$ . Wave functions using these combinations are labeled  $p_x$ ,  $p_y$ , and  $p_z$  ( $p$  because  $\ell = 1$ ).

Similarly for  $\ell = 2$ , one may write

$$C_2^0 = \frac{3}{2} \cos^2 \theta - \frac{1}{2} = \frac{1}{r^2} \left( z^2 - \frac{x^2 + y^2}{2} \right)$$

$$\frac{C_2^{-1} - C_2^1}{\sqrt{2}} = \sqrt{3} \sin \theta \cos \theta \cos \phi = \sqrt{3} \frac{xz}{r^2}$$

$$\frac{C_2^{-1} + C_2^1}{-\sqrt{2}i} = \sqrt{3} \sin \theta \cos \theta \sin \phi = \sqrt{3} \frac{yz}{r^2}$$

$$\frac{C_2^2 - C_2^{-2}}{\sqrt{2}i} = \frac{\sqrt{3}}{2} \sin^2 \theta \sin 2\phi = \sqrt{3} \frac{xy}{r^2}$$

$$\frac{C_2^{-2} + C_2^2}{\sqrt{2}} = \frac{\sqrt{3}}{2} \sin^2 \theta \cos 2\phi = \frac{\sqrt{3}}{2} \frac{x^2 - y^2}{r^2}$$

These linear combinations are sometimes labeled  $d_{xy}$ ,  $d_{x^2-y^2}$ , etc. This labeling is not usually carried beyond  $\ell = 2$ . Such wave functions are often used for molecular orbital theory.

# Appendix C

## Some Tensor Background

A vector may be defined as any object which transforms like a coordinate point

$$A'_i = \lambda_{ij} A_j$$

A coordinate point transforms by coordinate rotation by

$$x'_i = \lambda_{ij} x_j$$

where  $\lambda_{ij} \equiv \cos(x'_i, x'_j)$ .

In  $n$ -dimensional space, an  $m$ th rank tensor is an object which transforms under coordinate rotations as

$$T'_{abcd\dots} = \lambda_{ai} \lambda_{bj} \lambda_{ck} \lambda_{dl} \dots T_{ijkl\dots}$$

It has  $n^m$  components. Such a Cartesian tensor has a rank given by the number of indices. In three dimensions, an  $\ell$ th-rank tensor has  $3^\ell$  components.

A symmetric tensor is invariant to the interchange of any two indices. For an  $\ell$ th-rank tensor, this reduces the number of components from  $3^\ell$  to  $(\ell+1)(\ell+2)/2$ . (Can you show this?) For example, a 4th rank tensor is reduced from 81 to 15 components.

Now a second rank tensor is traceless whenever

$$\delta_{ij} T_{ij} = 0 \quad \text{or} \quad T_{11} + T_{22} + T_{33} = 0$$

The generalization of this is that

$$\delta_{mn} T_{ijk\dots\ell} = 0$$

where  $m$  and  $n$  are *any* two indices. Such a tensor is said to be irreducible and has only  $(2\ell + 1)$  independent components. So a 4th rank tensor which started with 81 components would have only 9.

Most tensors which describe physical phenomena are symmetric, and by being clever, one can usually make them irreducible.

Consider, for example, an electrostatic multipole moment. You may recall that the quadrupole moment is defined as

$$Q_{ij} = \frac{1}{2} \int \rho(\vec{r}') (3x'_j x'_i - r'^2 \delta_{ij}) d\tau'$$

The  $2^{\text{th}}$  pole moment is defined as

$$Q_{ijk\dots\ell} \equiv \frac{(-1)^\ell}{\ell!} \int \rho(\vec{r}') r'^{(2\ell+1)} \nabla'_i \nabla'_j \nabla'_k \dots \nabla'_\ell \left( \frac{1}{r'} \right) d\tau'.$$

Such a moment satisfies  $\delta_{mn} Q_{ijk\dots\ell} = 0$  and is symmetric.

Recall that for  $Y_\ell^m$   $m$  ranges from  $-\ell$  to  $\ell$  and takes on  $(2\ell + 1)$  values. In this way  $Y_\ell^m$  can be used as a *basis* for irreducible tensors or spherical tensors. The spherical tensor analog of  $Q_{ijk\dots\ell}$  is

$$q_{\ell m} \equiv \int Y_\ell^{*m}(\theta', \phi') r'^\ell \rho(\vec{r}') d\tau'$$



# Appendix D

## Magnetic Dipole Interaction Energy

Recall that the definition of the magnetic dipole,  $\vec{\mu}$ , of a current distribution is

$$\vec{\mu} \equiv \frac{1}{2c} \int \vec{r}' \times \vec{J}(\vec{r}') d\tau'$$

But

$$\vec{J} = Nq\vec{v} = N \frac{q}{m} \vec{p}$$

where  $N$  is the number of particles (of mass  $m$  and charge  $q$ ) per unit volume and  $\vec{p}$  is the momentum. So

$$\vec{\mu} = \frac{Nq}{2cm} \int (\vec{r}' \times \vec{p}') d\tau'$$

If there is but one particle in a volume  $V$  with charge  $q = -e$  whose angular momentum is a constant of the motion, the dipole moment may be written as

$$\vec{\mu} = -\frac{e\vec{\ell}}{2cmV} \int d\tau' = -\frac{e\vec{\ell}}{2mc} \tag{D.1}$$

The interaction energy (potential energy) of a magnetic dipole moment in an external magnetic field is what is desired. (The analogous result for an electric dipole in an external electric field is  $-\vec{p} \cdot \vec{E}$ .) Expand the magnetic field about some suitable origin:

$$B_i(\vec{r}) = B_i(0) + \vec{r} \cdot \vec{\nabla} B_i(0) + \dots \tag{D.2}$$

Now the force on a current distribution in an external field is

$$\vec{F} = \frac{1}{c} \int \vec{J}(\vec{r}') \times \vec{B}(\vec{r}') d\tau' \tag{D.3}$$

(This is just an extension of the Lorentz law,  $\vec{F} = (q/c)\vec{v} \times \vec{B}$ .) Putting (D.2) into (D.3) gives

$$\vec{F} = \frac{-1}{c} \vec{B}(0) \times \int \vec{J}(\vec{r}') d\tau' + \frac{1}{c} \int \vec{J}(\vec{r}') \times [(\vec{r}' \cdot \vec{\nabla}) \vec{B}(0)] d\tau' + \dots$$

The first term is zero for steady-state localized currents. Next note that

$$\vec{J}(\vec{r}') \times [(\vec{r}' \cdot \vec{\nabla})\vec{B}] = \vec{J}(\vec{r}') \times \vec{\nabla}(\vec{r}' \cdot \vec{B})$$

This follows by the vector identity

$$\vec{\nabla}(\vec{r}' \cdot \vec{B}) = \vec{r}' \times (\vec{\nabla} \times \vec{B}) + \vec{B} \times (\vec{\nabla} \times \vec{r}') + (\vec{r}' \cdot \vec{\nabla})\vec{B} + (\vec{B} \cdot \vec{\nabla})\vec{r}'$$

However,  $\vec{\nabla} \times \vec{B} = 0$  and  $\nabla$  do not operate on primed variables, so only the third term on the RHS is nonzero. Next note that

$$\vec{\nabla} \times (\vec{r}' \cdot \vec{B})\vec{J} = (\vec{r}' \cdot \vec{B})\vec{\nabla} \times \vec{J}(\vec{r}') + \vec{\nabla}(\vec{r}' \cdot \vec{B}) \times \vec{J}(\vec{r}')$$

This is a vector identity and the first term of the RHS is zero because  $\nabla$  does not operate on  $\vec{J}(\vec{r}')$ . So

$$\vec{F} = -\frac{1}{c}\vec{\nabla} \times \int \vec{J}(\vec{r}')(\vec{r}' \cdot \vec{B}(0)) d\tau' \quad (\text{D.4})$$

Now use the identity

$$\vec{B} \times (\vec{r}' \times \vec{J}') = \vec{r}'(\vec{B} \cdot \vec{J}') - \vec{J}'(\vec{r}' \cdot \vec{B})$$

to express the integral as

$$\int \vec{J}(\vec{r}')(\vec{r}' \cdot \vec{B}) d\tau' = \int \vec{r}'(\vec{B} \cdot \vec{J}') d\tau' - \vec{B} \times \int (\vec{r}' \times \vec{J}') d\tau' \quad (\text{D.5})$$

On the LHS, there is

$$B_i \int J'_j x'_i d\tau' = B_i \int [\nabla'_\ell(x'_j J'_\ell)] x'_i d\tau'$$

(This is easy to get by working on the right to obtain the left.) Now integrate the RHS by parts:

$$\begin{aligned} &= -B_i \int x'_j J'_\ell \nabla'_\ell x'_i d\tau' \\ &= -B_i \int x'_j J'_i d\tau' \\ &= - \int \vec{r}'(\vec{B} \cdot \vec{J}') d\tau' \end{aligned}$$

So the first term on the RHS of (D.5) is the negative of the LHS. (D.5) becomes

$$\int \vec{J}(\vec{r}')(\vec{r}' \cdot \vec{B}) d\tau' = -\frac{1}{2}\vec{B} \times \int (\vec{r}' \times \vec{J}') d\tau'$$

Putting this into (D.4) gives

$$\begin{aligned}\vec{F} &= \vec{\nabla} \times \left[ \vec{B} \times \frac{1}{2c} \int (\vec{r}' \times \vec{J}') d\tau' \right] \\ \text{or } \vec{F} &= \vec{\nabla} \times (\vec{B} \times \vec{\mu})\end{aligned}\tag{D.6}$$

Now use the vector identity

$$\begin{aligned}\vec{\nabla} \times (\vec{A} \times \vec{B}) &= \vec{A}(\vec{\nabla} \cdot \vec{B}) - \vec{B}(\vec{\nabla} \cdot \vec{A}) + (\vec{B} \cdot \vec{\nabla})\vec{A} - (\vec{A} \cdot \vec{\nabla})\vec{B} \\ \text{and } \vec{F} &= (\vec{\mu} \cdot \vec{\nabla})\vec{B} = \vec{\nabla}(\vec{\mu} \cdot \vec{B})\end{aligned}\tag{D.7}$$

remembering that  $\vec{\mu}$  is a constant vector and that  $\text{div } \vec{B} = \text{curl } \vec{B} = 0$ .

So if  $\vec{F} = -\vec{\nabla}W$  where  $W$  is the potential energy, it follows that

$$W = -\vec{\mu} \cdot \vec{B}\tag{D.8}$$

# Index

## A

Absorption, 100, 110–112  
 $A^k$ , 61, 62  
 $\alpha$  fine-structure constant, 14  
Alternating unit tensor, 4  
Angular momentum, 6, 23, 46–48  
Anharmonic oscillator, 146–149  
Anharmonic vibration, 148  
Anomalous Zeeman effect, 84  
Anti-bonding orbitals, 137–138  
Anticommutator, 25  
Antisymmetric, 44  
Antisymmetrization operator, 44  
Associated Laguerre polynomials, 16  
Atomic units, 14  
Average energy of a configuration, 67

## B

Bohr magneton, 82  
Bohr radius, 15  
Bonding orbital, 137–138  
Born–Oppenheimer  
  approximation, 116–117, 140  
  separation, 146  
Bosons, 155

## C

Center of mass, 140  
Central potential, 42  
Clebsch–Gordan coefficients (C-G'S), 28, 30, 60, 75  
Cm-1, 16  
Coefficient  $c^k$ , 60  
Commutator, 5

Correlation energy, 133

Coulomb  
  integral, 58  
  potential, 13

## D

Degeneracy, 20, 50  
Determinantal equation, 87  
Dipole moment, 150  
Dirac delta function, 97  
Dissociation energy, 145  
Dummy, 4

## E

Eigenstate of hydrogen, 19  
Einstein A coefficient, 110  
Einstein B coefficient, 110  
Einstein summation convention, 4  
Electric dipole  
  approximation, 102  
  transition, 107  
Electric multipole moment, 107  
Electron probability density, 122  
Electron volt (eV), 15  
Emission, 100  
Energy density, 100  
Equivalent electrons, 49–51  
Exchange  
  integral, 58, 61  
  interaction, 63

## F

Fermi contact term., 91  
Fermions, 44, 155

Fermi's golden rule, 97  
 Fine structure, 35, 73–80  
 $F^k$ , 61, 62  
 Franck–Condon factor, 151

**G**

Generalized angular momentum, 27  
 Gerade, 118  
 $G^k$ , 61  
 Grotrian level diagram, 16

**H**

$H_2^+$ , 117  
 Hamiltonian, 9, 27, 35, 42  
 Harmonic interaction, 98  
 Hartree, 14–15  
 Hartree–Fock  
   procedure, 41  
   equations, 68–72  
 Hermite polynomials, 145  
 Hilbert space, 11, 23–25, 27, 28  
 Homonuclear molecules, 118  
 Hönl–London factor, 151, 152  
 Hund's rule, 65  
 Hydrogen  
   atom, 17  
   molecular ion, 116–129  
   molecule, 129–134  
 Hyperfine structure, 89–92

**I**

Indicial notation, 3–5  
 Indistinguishability, 44  
 Internuclear axis, 118  
 Internuclear separation, 117  
 Inversion  
   of coordinates, 157  
   symmetry, 134  
 Ionization energies, 36  
 Isoelectronic sequence, 64

**J**

3- $j$  symbols, 31, 60

**K**

Koopman's theorem, 69

**L**

$L_+$ , 11  
 $L_-$ , 11  
 Ladder operators, 11, 75  
 Lambda doubling, 156  
 Landé  
   approximation, 78  
    $g$ -value, 83  
   interval rule, 79  
 Levels, 47  
 Lifetime, 103–106  
 Linear combination of atomic orbitals (LCAO),  
   119, 127  
 Linear Stark effect, 86–87  
 Line strength, 110  
 LS coupling, 46

**M**

Magnetic  $g$ -factor, 81  
 Magnetic moment, 81  
 Matrix elements, 35  
 Matrix mechanics, 21  
 Maxwell–Boltzmann distribution, 152  
 Molecular orbitals (MO), 117–119, 123  
 Moment of inertia, 144  
 Morse potential, 146  
 Multiplicity, 47

**N**

Non-rigid rotator, 146–149  
 Nuclear spin, 155–159  
 Nuclear spin statistics, 160

**O**

Occupation number, 58  
 Off-diagonal matrix elements, 55  
 One-electron operator, 53–56  
 Orbital, 27  
 Ortho, 157  
 Orthogonality relations, 31  
 Oscillator strength, 108–110  
 Overlap probability, 122

**P**

Para, 157  
 Parent terms, 47  
 Parity, 48, 109

- Partition function, 152
- Pauli
- exclusion principle, 49
  - principle, 44
  - spin matrices, 26
- P-branch, 160
- Potential energy
- curves, 117
  - operator, 124
- Q**
- Q-branch, 160
- Quadratic Stark effect, 86, 88–89
- R**
- Radial wave functions, 36
- R-branch, 160
- Rigid rotation, 148
- Rotational energy, 144
- Rotational partition function, 153
- Rotational selection rule, 151
- Russell–Saunders, 46
- Rydberg constant, 16
- Rydbergs, 14
- S**
- Schrödinger equation, 34
- Selection rules, 109, 111, 149–152, 159
- Self-consistent field, 42, 69
- Separated atom limit, 119–120
- Shell
- model, 42–46
  - structure, 45
- Simple harmonic oscillator, 145
- Slater
- determinants, 44, 49
  - sum rule, 63
- Spherical coordinates, 9, 143
- Spherical harmonic addition theorem, 59
- Spherical harmonic functions, 36, 38
- Spherical harmonics, 10
- Spherical tensors, 32
- Spheroidal coordinates, 117
- Spin
- angular momentum, 20–27
  - orbital, 27
  - wave functions, 156
- Spinor, 130
- Spontaneous emission, 98–103
- Stark effect, 74, 85–89
- State, 47
- designations, 134
  - sum, 152
- Statistical weight, 157
- Stern–Gerlach experiment, 24
- Sturm–Liouville problem, 10
- Symmetric, 43
- Symmetrization operator, 44
- T**
- Terms, 47
- Thermal distribution, 152–155
- Time dependent perturbation theory, 93–98
- Total energy, 125
- Total spin, 157
- Transition(s), 149–152
- moments, 106–108
  - probabilities, 93–112
- 21 cm line, 91
- Two-electron operators, 56–62
- U**
- Ungerade, 118
- Unitary matrix, 28
- United atom limit, 119–120
- V**
- Variational calculation, 120–129
- Variation technique, 51
- Vector-coupling coefficients, 28
- W**
- Wave mechanics, 21
- Wigner–Eckart theorem, 32
- Y**
- Yrast transition, 108
- Z**
- Zeeman effect, 24, 74, 80–85