Reference Material on Atomic Molecular and Optical Physics

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Contents

1 Basics

1.1 Nonrelativistic quantum mechanics

Schrödinger equation:

$$i\frac{\partial}{\partial t}\Psi = H\Psi \tag{1}$$

$$H = -\frac{\hbar^2}{2m}\Delta + V \tag{2}$$

Linear momentum

$$\hat{\mathbf{p}} = -i\hbar\nabla$$

Probability current density

$$\mathbf{j} = \frac{1}{2m}\left(\Psi(\mathbf{p}\Psi)^* + \Psi^*\mathbf{p}\Psi\right)$$

Time-evolution of expectation values

$$i\hbar\frac{d}{dt}\langle F\rangle_t = \langle[F,H]\rangle_t + i\hbar\langle\frac{\partial F}{\partial t}\rangle_t$$

Commutator identities

$$[p_i, r_j] = -i\hbar\delta_{ij}$$

1.2 Harmonic oscillator

$$\begin{aligned}
H &= \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2 \\
E_n &= \hbar\omega\left(n + 1/2\right) \\
|\phi_n\rangle &= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\frac{1}{\sqrt{2^n 2!}}H_n\left(x\sqrt{\frac{m\omega}{\hbar}}\right)\exp\left[-\frac{1}{2}\frac{m\omega}{\hbar}x^2\right]
\end{aligned}$$

Creation and annihilation operators

$$\begin{aligned}
a &= \sqrt{\frac{m\omega}{2\hbar}}\left(x + i\frac{p}{m\omega}\right) \\
a^\dagger &= \sqrt{\frac{m\omega}{2\hbar}}\left(x - i\frac{p}{m\omega}\right) \\
x &= \sqrt{\frac{\hbar}{2m\omega}}\left(a + a^\dagger\right) \\
p &= i\sqrt{\frac{\hbar m\omega}{2}}\left(a^\dagger - a\right) \\
a|n\rangle &= \sqrt{n}|n-1\rangle \\
a^\dagger|n\rangle &= \sqrt{n+1}|n+1\rangle \\
|n\rangle &= \frac{1}{\sqrt{n!}}\left(a^\dagger\right)^n|0\rangle
\end{aligned}$$

Various matrix elements

$$\langle n|x|k\rangle = \sqrt{\frac{\hbar}{m\omega}}\left\{\sqrt{\frac{n}{2}}\delta_{k,n-1} + \sqrt{\frac{n+1}{2}}\delta_{k,n+1}\right\}$$

$$\langle n|x^2|n\rangle = \frac{\hbar}{m\omega}\left(n+1/2\right)$$

$$\langle n+2|x^2|n\rangle = \frac{\hbar}{m\omega}\frac{1}{2}\left\{\left(n+1\right)\left(n+2\right)\right\}^{1/2}$$

$$\langle n-2|x^2|n\rangle = \frac{\hbar}{m\omega}\frac{1}{2}\left\{n\left(n-1\right)\right\}^{1/2}$$

1.3 Feynman diagrams and propagators

Solution through the **propagator**

$$\psi(x',t) = \int_{-\infty}^{\infty} D_F(x',t;x,0)\,\psi(x,0)$$

Free particle propagator

$$D_F^{(0)}(x',t;x,0) = \theta(t)\sqrt{\frac{m}{2\pi i t}}\,\exp\left(i\frac{m(x'-x)^2}{2t}\right)$$

Feynman *path integral*

$$D_F(x',t;x,0) = \int \mathrm{D}[x(t)]\,\exp\frac{iS[x(t)]}{\hbar}$$

summation is over all paths $x(t)$ connecting the initial $(x,0)$ and final (x',t) points, $S[x(t)]$ is a classical action along a given path $x(t)$

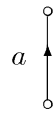
$$S[x(t)] = \int_{x_1}^{x_2} dt\left(\frac{1}{2}m\dot{x}^2(t) - V(x(t))\right)$$

Spectral decomposition in terms of H eigenfunctions :

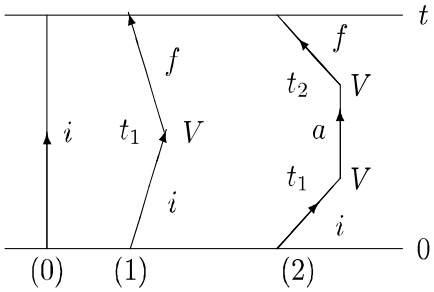
$$D_F(x',t;x,0) = \sum_n \phi_n(x')\phi_n(x)e^{-iE_n t}$$

The transition amplitude $\mathrm{Amp}_{fi} = \langle f|U(t,0)|i\rangle$ is expressed as a sum of all possible pathes :

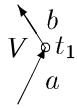
In this picture :



$$= \exp\left(-iE_a(t_2-t_1)\right)$$



and each vertex is associated with



$$= (-i)\langle b|V|a\rangle dt_1$$

For example the second order expression is

$$\mathrm{Amp}_{fi}^{(2)}(t) = \sum_a \int_0^{t_2} \int_0^t e^{-iE_i(t_1-0)}(-i)V_{ai}dt_1 e^{-iE_a(t_2-t_1)}(-i)V_{fa}dt_2 e^{-iE_f(t-t_2)}$$

1.4 Pauli matrices ($\hat{s} = 1/2\ \hat{\sigma}$)

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Identities with Pauli matrices

$$\begin{aligned} \sigma_i\sigma_j &= \delta_{ij} + i\varepsilon_{ijk}\sigma_k \\ (\sigma\cdot\mathbf{A})(\sigma\cdot\mathbf{B}) &= (\mathbf{A}\cdot\mathbf{B}) + i\sigma(\mathbf{A}\times\mathbf{B}) \\ \sigma(\sigma\cdot\mathbf{A}) &= \mathbf{A} - i(\sigma\times\mathbf{A}) \\ (\sigma\cdot\mathbf{A})\sigma &= \mathbf{A} + i(\sigma\times\mathbf{A}) \end{aligned}$$

Rotation matrix [active rotation about axis $\hat{n}$ on angle ϕ]

$$U_R = \cos\frac{\phi}{2} - i\hat{n}\cdot\sigma\sin\frac{\phi}{2}$$

Density matrix $\rho = |\chi\rangle\langle\chi|$ and polarization vector $\mathbf{P} = \langle\chi|\,\sigma\,|\chi\rangle$

$$\rho = \frac{1}{2}(1 + (\mathbf{P}\cdot\sigma))$$

2 Dirac equation

$$H_D = c\alpha \cdot \mathbf{p} + \beta c^2 + V(r)$$
$$\alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix} \quad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Current density (Below q is a charge, for electron $q = -|e|$)

$$\mathbf{j}(r) = qc \int \Psi^\dagger \alpha \delta(r - r') \Psi dr'$$

Interaction with the EM field

$$H_I = -qc\alpha \cdot \mathbf{A} + q\phi$$

2.1 Four-vectors

Contra-variant symbols

$$x^\mu = (t, \mathbf{r})$$
$$p^\mu = (E, \mathbf{p})$$

co-variant symbols

$$x_\mu = \eta_{\mu\nu} x^\nu = (t, -\mathbf{r})$$
$$p_\mu = \eta_{\mu\nu} p^\nu = (E, -\mathbf{p})$$

with metric tensor

$$\eta_{\mu\nu} = \begin{pmatrix} 1 & & & 0 \\ & -1 & & \\ & & -1 & \\ 0 & & & -1 \end{pmatrix}$$

Contraction (Lorentz invariant)

$$A^\mu B_\mu = A_\mu B^\mu = A_\mu B_\mu \eta_{\mu\nu} = A^0 B^0 - \mathbf{A} \cdot \mathbf{B}$$

Momentum operator

$$p^\mu = i \frac{\partial}{\partial x_\mu} = i\partial^\mu = i\nabla^\mu = i\left(\frac{\partial}{\partial t}, -\nabla\right)$$

$\partial^\mu A_\mu$ is a Lorentz invariant.

2.2 Dirac matrices

$$\gamma_0 = \begin{pmatrix} 1_{2\times 2} & 0 \\ 0 & -1_{2\times 2} \end{pmatrix} \qquad \gamma^i = \begin{pmatrix} 0 & \sigma_i \\ -\sigma_i & 0 \end{pmatrix}$$

$$\gamma^\mu \gamma^\nu + \gamma^\nu \gamma^\mu = 2\eta^{\mu\nu}$$

$$\gamma_5 = -i\gamma^0\gamma^1\gamma^2\gamma^3$$

$$\sigma^{\mu\nu} = \frac{i}{2}\left[\gamma^\mu, \gamma^\nu\right]$$

γ_5 differs from Ref.[BD64] by the "-" sign. Slash shorthand

$$\not{a} = \gamma^\mu a_\mu = \gamma^0 A^0 - \gamma \cdot \mathbf{A}$$

Dirac equation (spin 1/2)

$$\left(i \not{\partial} - e \not{A} - m\right)\psi(x) = 0$$

Klein-Gordon equation (spin 0)

$$\left\{(i\partial - eA)_\mu (i\partial - eA)^\mu - m^2\right\}\psi(x) = 0$$

3 Units and conversions

Fundamental constants

$$\begin{aligned} \hbar &= 1.054571596 \times 10^{-34}\ J\ s \\ h &= 6.62606876 \times 10^{-34}\ J\ s \\ m_e &= 9.10938188 \times 10^{-31}\ kg \\ |e| &= 1.602176462 \times 10^{-19}\ C \\ k_B &= 1.3806503 \times 10^{-23}\ J/K \\ \alpha &= \frac{e^2}{\hbar c} = 1/137.03599976 \end{aligned}$$

Atomic units $m_e = \hbar = |e| = 1$

$$a_0 = \frac{\hbar^2}{m_e e^2} = 0.529177249 \times 10^{-8}\text{cm} \approx 0.5\text{Å}$$
$$1\text{fm} = 10^{-13}\text{cm} = 1.88973 \times 10^{-5}\text{bohr}$$
$$1\text{barn} = \ 10^{-28}\ \text{m}^2$$
$$\frac{1}{4\pi\varepsilon_0} = 1 \text{ a.u.(Gaussian)}$$
$$\frac{\mu_0}{4\pi} = \alpha^2 \text{ a.u.(Gaussian)}$$
$$\mu_B = \frac{|e|\,\hbar}{2m_e} = \frac{1}{2}\text{a.u. Bohr magneton (in SI)}$$
$$\mu_B = \frac{|e|\,\hbar}{2m_e c} = \frac{\alpha}{2}\text{a.u. Bohr magneton (in Gaussian)}$$
$$1a.u.\text{of time} = \hbar/E_h = 2.4188843265 \times 10^{-17}s$$

$$\lambda_e = \frac{h}{m_e c} = 2.4263\ \times 10^{-10}\text{cm} \quad \text{Compton wavelength}$$
$$\lambda\!\!\!^{-}_e = \frac{\hbar}{m_e c} \approx 386\text{ fm} \quad \text{reduced Compton wavelength}$$
$$E = \frac{e^2}{a_0} = 0.51422082 \times 10^{12}\frac{\text{V}}{\text{m}} \quad \text{Electric field}$$
$$B = \frac{E_h}{e a_0 \alpha c} = 2.350518\ \times 10^5 \text{ tesla} = 2.350518\ \times 10^9 \text{ Gauss Magnetic field}$$

Energy:

$$1\text{Hartree} \equiv 1\text{a.u.} = \frac{e^2}{a_0} = 4.3597438110 \times 10^{-18}J$$
$$1\text{Rydberg} \equiv 0.5\text{a.u.}$$
$$1\,\text{cm}^{-1} = 4.556335252750(35) \times 10^{-6}\text{a.u.}$$
$$1\text{eV} = 3.67493260(14) \times 10^{-2} \text{ a.u.}$$
$$1\text{K} = 3.1668153(55) \times 10^{-6} \text{ a.u.}$$
$$1\,\text{cm}^{-1} = 1.4387752\,\text{K}$$
$$1\text{a.u.} = 6.579683920735(50) \times 10^{15}\text{Hz (Notice that this is } \nu \text{ not } \omega = 2\pi\nu)$$

EM Fields and laser intensity

$$\mathcal{E}_0 = \frac{e^2}{a_0} = m^2 e^5/\hbar^4 = 5.14220826 \times 10^9\ V/cm$$
$$\mathcal{B} = \frac{E_h}{e a_0 \alpha c} = 2.350518\ \times 10^5 \text{ tesla} \quad \text{Magnetic field}$$
$$I_0 = \mathcal{E}_0^2 = XXX\ W/cm^2$$

Conversions :

$$\lambda(\text{Å}) = a_0 \frac{2\pi c}{\Delta E(\text{a.u.})} \times 10^8 = \frac{455.634}{\Delta E(\text{a.u.})}$$
$$\lambda(\text{nm}) = \frac{45.5634}{\Delta E(\text{a.u.})}$$
$$\lambda(\text{cm}^{-1}) = \frac{1}{a_0}\frac{1}{2\pi c}\Delta E(\text{a.u.}) = 219475\ \Delta E(\text{a.u.})$$

Misc units

$$1\ \text{Tesla} = 10^4\ \text{Gauss}$$
$$m_p = 1836.1526675\ m_e$$

3.1 Natural units

$\hbar = c = 1$, in QED in addition $m_e = 1$.

3.2 Systems of units in electrodynamics

After Ref.[GR02], Supplement 4.2.

Three system of units: Gaussian, MKSA (part of SI), and Heaviside-Lorentz ("rationalized Gaussian system"). Coulomb's law:

$$\mathbf{F} = k_1 \frac{q_1 q_2}{r^3}\mathbf{r}$$
$$k_1^G = 1$$
$$k_1^{MKSA} = \frac{1}{4\pi\varepsilon_0}$$
$$k_1^{HL} = \frac{1}{4\pi}$$

if the unit of charge is fixed (it depends on a system of units), then the k_1 is defined from mechanical force.

Ampere's force law

$$\mathbf{F} = k_2 \int\int dr_1 dr_2 \frac{\mathbf{j}_1 \times (\mathbf{j}_2 \times \mathbf{r}_{12})}{r_{12}^3}$$

Units of charge density and current density are related via (system-of-units-independent) continuity equation

$$\nabla \cdot \mathbf{j} + \frac{\partial \rho}{\partial t} = 0$$

The convention is to fix $k_1/k_2 = c^2$, leading to

$$\begin{aligned} k_2^G &= \frac{1}{c^2} \\ k_2^{MKSA} &= \frac{\mu_0}{4\pi} \\ k_2^{HL} &= \frac{1}{4\pi c^2} \end{aligned}$$

Lorentz force on a moving charge

$$\mathbf{F} = q\left(\mathbf{E} + k_3 \frac{\mathbf{v}}{c} \times \mathbf{B}\right)$$

fixes units of electric and magnetic fields.

$$\begin{aligned} k_3^G &= k_3^{HL} = 1 \\ k_3^{MKSA} &= c \end{aligned}$$

The Maxwell's equations

$$\begin{aligned} \nabla \cdot \mathbf{E} &= 4\pi k_1 \rho \\ \nabla \cdot \mathbf{B} &= 0 \\ \nabla \times \mathbf{E} &= -\frac{k_3}{c}\frac{\partial \mathbf{B}}{\partial t} \\ k_3 \nabla \times \mathbf{B} &= \frac{4\pi k_1}{c}\mathbf{j} + \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t} \end{aligned}$$

Units of electric and magnetic potentials $k_4^G = k_4^{MKSA} = 1$

$$\begin{aligned} \mathbf{E} &= -\nabla\varphi - \frac{k_3}{c}\frac{\partial \mathbf{A}}{\partial t} \\ B &= k_4 \nabla \times \mathbf{A} \end{aligned}$$

4 Atomic Hamiltonian

Non-relativistic

$$H = -\sum_i \frac{1}{2}\nabla^2 - \sum_i \frac{Z}{r_i} + \frac{1}{2}\sum_{ij}\frac{1}{r_{ij}} \tag{3}$$

Relativistic

$$H = \sum_i \left(c\alpha_i \cdot \mathbf{p}_i + \beta_i c^2 + V_{\text{nuc}}(r_i)\right) + \Lambda_{++}\frac{1}{2}\sum_{ij}\frac{1}{r_{ij}}\Lambda_{++} \tag{4}$$

Breit interaction - static limit :

$$b_{12} = -\frac{1}{2r_{12}}(\alpha_1 \cdot \alpha_2 + \alpha_1 \cdot \hat{\mathbf{r}}_{12}\ \alpha_2 \cdot \hat{\mathbf{r}}_{12})$$

Alternative representation:

$$B = -(\ \alpha_{\mathbf{1}} \cdot \alpha_{\mathbf{2}}) \frac{1}{r_{12}} - \frac{1}{2}(\alpha_{\mathbf{1}} \cdot \nabla_{\mathbf{1}})(\alpha_{\mathbf{2}} \cdot \nabla_{\mathbf{2}}) r_{12}$$

Here the first term - Gaunt interaction, the second - retardation interaction.

4.1 Partial wave expansions of $1/r_{12}$ and r_{12}

Coulomb interaction:

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \frac{r_<^l}{r_>^{l+1}} P_l(cos\theta) = \sum_{lm}^{\infty} \frac{r_<^l}{r_>^{l+1}} (-1)^m C^l_{-m}(\hat{r}_1) C^l_m(\hat{r}_2)$$

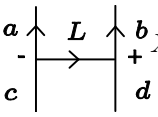
r_{12} is useful for Breit interaction expansion. This expression has been obtained from 10.1.46 of [AS74].

$$r_{12} = \sum_{lm} \left(\frac{1}{2l+3} \frac{r_<^{l+2}}{r_>^{l+1}} - \frac{1}{2l-1} \frac{r_<^l}{r_>^{l-1}} \right) (-1)^m C^l_{-m}(\hat{r}_1) C^l_m(\hat{r}_2)$$

4.2 Angular reduction of Coulomb interaction

$$g_{abcd} = \sum_{LM} (-1)^{L-M} (-1)^{j_a - m_a} \begin{pmatrix} j_a & L & j_c \\ -m_a & M & m_c \end{pmatrix} (-1)^{j_b - m_b} \begin{pmatrix} j_b & L & j_d \\ -m_b & -M & m_d \end{pmatrix} X_L(abcd)$$
$$= \sum_{LM} \frac{1}{\sqrt{[a]\,[d]}} C^{j_a m_a}_{j_c m_c, LM} C^{j_d m_d}_{LM, j_b m_b} X_L(abcd)$$

or

$$g_{abcd} = \sum_L$$ 

$$X_L(abcd)$$

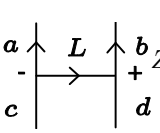
Here the Coulomb integral is

$$X_L(abcd) = (-1)^L \langle \kappa_a || C^{(L)} || \kappa_c \rangle \langle \kappa_b || C^{(L)} || \kappa_d \rangle R_L(abcd),$$

$R_k(abcd)$ being the Slater integral

$$R_L(abcd) = \int_0^\infty dr_1 [P_a(r_1) P_c(r_1) + Q_a(r_1) Q_c(r_1)] \int_0^\infty dr_2 \frac{r_<^L}{r_>^{L+1}} [P_b(r_2) P_d(r_2) + Q_b(r_2) Q_d(r_2).$$

The anti-symmetrized combinations $\tilde{g}_{abcd} = g_{abcd} - g_{abdc}$ are reduced in a similar way, except $X_k(abcd)$ is replaced with

$$\tilde{g}_{abcd} = \sum_L$$ 

$$Z_L(abcd),$$

with

$$Z_L(abcd) = X_L(abcd) + [L]\sum_{L'}\left\{\begin{array}{ccc} b & d & L \\ a & c & L' \end{array}\right\} X_{L'}(bacd)$$

Symmetry properties of X_k and Z_k

$$\begin{aligned} X_k(abcd) &= X_k(badc) \\ X_k(abcd) &= (-1)^{a-c} X_k(cbad) \\ X_k(abcd) &= (-1)^{a+b+c+d} X_k(cdab) \\ Z_k(abcd) &= Z_k(badc) \\ Z_k(abcd) &= (-1)^{a+b+c+d} Z_k(cdab) \end{aligned}$$

Recoupling

$$Z_L(ijkl) = [L]\sum_{L'}\left\{\begin{array}{ccc} j & l & L \\ i & k & L' \end{array}\right\} Z_{L'}(jikl)$$

$$Z_{L=0}(ijkl) = \delta_J(j,l)\,\delta_J(k,i)\,\frac{(-1)^{j+k}}{\sqrt{[j,k]}}\sum_{L'}(-1)^{L'} Z_{L'}(jikl)$$

Special case $L = 0$

$$X_{L=0}(abcd) = \delta_{\kappa_a\kappa_c}\delta_{\kappa_b\kappa_d}\sqrt{[j_a]\,[j_b]}R_L(abcd),$$

$$Z_{L=0}(abcd) = \delta_{\kappa_a\kappa_c}\delta_{\kappa_b\kappa_d}\sqrt{[j_a]\,[j_b]}R_L(abcd) + \sum_{L'}\frac{(-1)^{b+c+L'}}{\sqrt{[b,c]}}\delta_{bd}\delta_{ca}X_{L'}(bacd)$$

5 Hydrogenic ions

5.1 Non-relativistic hydrogenic ions

Wave function:

$$\psi(r) = \frac{1}{r}P(r)Y_{lm}(\hat{r}) \tag{5}$$

Radial equation:

$$\frac{d^2P}{dr^2} + 2(E - V(r) - \frac{l(l+1)}{2r^2})P = 0 \tag{6}$$

$$E_n = -\frac{Z^2}{2n^2}$$

$$\langle r\rangle \approx \frac{3n^2}{2Z}$$

5.2 Relativistic hydrogenic ions

Wave function are represented as Dirac bi-spinors :

$$u(\mathbf{r}) = \frac{1}{r}\begin{pmatrix} iP_{n\kappa}(r)\ \Omega_{\kappa m}(\hat{r}) \\ Q_{n\kappa}(r)\ \Omega_{-\kappa m}(\hat{r}) \end{pmatrix} = \frac{1}{r}\begin{pmatrix} iG_{n\kappa}(r)\ \Omega_{\kappa m}(\hat{r}) \\ F_{n\kappa}(r)\ \Omega_{-\kappa m}(\hat{r}) \end{pmatrix} \tag{7}$$

P(or G) -large , Q(or F) - small components. Notice that the notation G/F is reversed compared to traditional textbooks. Further, the spherical spinors $\Omega_{\kappa m}$ are coupled spherical harmonics $Y_{lm}(\hat{r})$ and spinors χ_μ of spin 1/2.

$$\Omega_{\kappa m} = \sum_\mu C(l, 1/2, j; m-\mu, \mu, m) Y_{l,m-\mu}\chi_\mu.$$

The radial Dirac equation

$$\left(V(r) + c^2\right) P_{n\kappa}(r) + c\left(\frac{d}{dr} - \frac{\kappa}{r}\right) Q_{n\kappa}(r) = \varepsilon_{n\kappa} P_{n\kappa}(r)$$
$$-c\left(\frac{d}{dr} + \frac{\kappa}{r}\right) P_{n\kappa}(r) + \left(V(r) - c^2\right) Q_{n\kappa}(r) = \varepsilon_{n\kappa} Q_{n\kappa}(r)$$

with the normalization

$$\int_0^\infty \left[P_{n\kappa}^2(r) + Q_{n\kappa}^2(r)\right] dr = 1.$$

In the non-relativistic limit (Pauli approximation)

$$Q_{n\kappa} \approx -\frac{1}{2c}\left(\frac{d}{dr} + \frac{\kappa}{r}\right) P_{n\kappa}\ .$$

Hydrogenic ion energy levels:

$$E_{nk} = \frac{c^2}{\sqrt{1 + (\alpha Z)^2/(\gamma + n - k)^2}} \approx c^2 - \frac{Z^2}{2n^2} - \frac{\alpha^2 Z^4}{2n^2}(1/k - 3/(4n)) \tag{8}$$

with $\gamma = \sqrt{k^2 - (\alpha Z)^2}$.

κ, relativistic angular quantum number: $|\kappa| = j + 1/2, \kappa < 0$ if $j = l + 1/2, \kappa > 0$ if $j = l - 1/2$. Another form $\kappa = \left(j + \frac{1}{2}\right)(-1)^{j+l+1/2}$ or $\kappa = (l - j)(2j + 1)$. Notice $\kappa(\kappa + 1) = l(l + 1)$.

l	j	κ	l	j	κ
s	1/2	-1			
p	1/2	1	f	5/2	3
p	3/2	-2	f	7/2	-4
d	3/2	2	g	7/2	4
d	5/2	-3	g	9/2	-5

5.3 Atomic wave-functions in the limit $r \to 0$

(After [Dra96] Ch.22, notice different convention for P/Q definitions. Here we use the definition (7)). Here the energy E excludes the rest mass energy $m_e c^2$.

Finite nucleus. For $\kappa < 0$

$$\begin{aligned} P_\kappa &\approx p_0 r^{l+1} \\ Q_\kappa &= q_1 r^{l+2} \\ \frac{q_1}{p_0} &= -\left(E + Z_1\right) / \left(c\left(2l+3\right)\right) \end{aligned}$$

and for $\kappa > 0$

$$\begin{aligned} P_\kappa &\approx p_1 r^{l+1} \\ Q_\kappa &= q_0 r^{l} \\ \frac{p_1}{q_0} &= \left(E + Z_1\right) / \left(c\left(2l+1\right)\right) \end{aligned}$$

Here Z_1 is the expansion coefficient in

$$\begin{aligned} V\left(r\right) &= -\frac{Z\left(r\right)}{r} \\ Z\left(r\right) &= \sum_{n=0}^{\infty} Z_n r^n \end{aligned}$$

For a uniform distribution $Z_1 = 0$.

5.4 Scalings

Non-relativistic energies in the nuclear Coulomb potential	Z^2
e-e Coulomb interaction	Z
Relativistic energy corrections	$(\alpha Z)^2 Z^2$
Relativistic corrections to e-e interaction	$(\alpha Z)^2 Z$
Breit interaction caused by transverse photons	$(\alpha Z)^2 Z$
QED effects (Lamb shift)	$(\alpha Z)^3 Z$
Virtual pairs	$(\alpha Z)^3 Z$ or sometimes $(\alpha Z)^3$

5.5 Matrix elements

see Bethe and Salpeter

$$\langle n, l-1, m | z | n, l, m \rangle = -\frac{3}{2} n a_0 \sqrt{n^2 - l^2} \;\times\; \sqrt{\frac{l^2 - m^2}{\left(2l+1\right)\left(2l-1\right)}},$$

6 Hartree-Fock equations

One typically distinguishes between "restricted" and "unrestricted" Hartree-Fock method. The unrestricted HF is the method when the many-body wavefunction is approximated by a Slater determinant composed of single-particle orbitals. When the energy functional of the system is minimized with respect to the shape of these orbitals, one obtains a set of coupled equations (Ref. [Mer98])

$$V_{\rm HF}\left|m\right\rangle = \sum_{p=1}^{\infty}\left|p\right\rangle \sum_{a\in{\rm occ}}\left(\left\langle pa\right|V\left|ma\right\rangle - \left\langle pa\right|V\left|am\right\rangle\right)$$
$$\left(T+V_{\rm HF}\right)\left|m\right\rangle = \varepsilon_m\left|m\right\rangle$$

The restricted HF (traditional in atomic physics) in addition assumes the central-field character of the resulting potential, so that the orbitals are the eigenfunctions of the total momentum operator J and J_z (nonrelativistic and relativistic) and only the radial components are varied.

Non-relativistic equations, closed-shell system:

$$-\frac{1}{2}\frac{d^2P_a}{dr^2} + \left(V_{\rm HF} - \frac{Z}{r} + \frac{l_a(l_a+1)}{2r^2}\right)P_a(r) = \varepsilon_a P_a(r)$$

Here

$$\hat{V}_{\rm HF}P(r) = \hat{V}_{\rm dir}P(r) + \hat{V}_{\rm exc}P(r)$$
$$\hat{V}_{\rm dir}P(r) = \left(2\sum_b [l_b]v_0(b,r)\right)P(r)$$
$$\hat{V}_{\rm exc}P_{n_al_a}(r) = -2\sum_b [l_b]\sum_L \Lambda_{l_bLl_a}\,v_{l'}(b,a,r)P_{n_bl_b}(r)$$
$$\Lambda_{l_aLl_b} = \frac{1}{2}\begin{pmatrix} l_a & L & l_b \\ 0 & 0 & 0\end{pmatrix}^2$$
$$v_l(a,b,r) = \int_0^\infty dr'\left(\frac{r_<^l}{r_>^{l+1}}\right)P_a(r')\,P_b(r')$$
$$v_0(a,r) = \int_0^\infty dr'\frac{1}{r_>}\left|P_a(r')\right|^2$$

Relativistically

$$\Lambda_{\kappa_aL\kappa_b} = \begin{pmatrix} j_a & j_b & L \\ -1/2 & 1/2 & 0\end{pmatrix}^2 \Pi\left(l_a+L+l_b\right)$$
$$\Lambda_{\kappa_a0\kappa_b} = \frac{\delta_{\kappa_a\kappa_b}}{[j_a]}$$

For a valence system the potential is taken as the frozen core potential $V_{\rm HF}$ Frozen-core Hartree-Fock

$$(V_{\rm HF})_{ij} = \sum_{a\in{\rm core}}\tilde{g}_{iaja}\,.$$

Angular reduction (relativistic case):

$$(V_{\mathrm{HF}})_{ij} = \frac{\delta_{\kappa_i \kappa_j}}{\sqrt{[i]}} \sum_{a \in \mathrm{core}} \sqrt{[a]} Z_0(iaja)\,.$$

6.1 Multi-configurational Hartree-Fock (MCHF)

Multi-configurational Hartree-Fock. A number of configurations is mixed with coefficients. Minimize the energy, both radial functions and mixing coefficients are subject to variations.(CI varies only mixing coefficients - the basis set must be complete)

7 Coupling to EM field

Gaussian

$$V = -q\ \left(\alpha \cdot \mathbf{A}^{\mathrm{G}}\right)$$

SI

$$V = -cq\ \left(\alpha \cdot \mathbf{A}^{\mathrm{SI}}\right)$$

An interaction of an electron with EM field (here $e > 0$). We use SI/MKSA units

$$V_L = ce\left(\alpha \cdot \mathbf{A}\left(r,t\right)\right) - e\Phi\left(r,t\right)$$

For EM wave in the transverse gauge, the scalar potential $\Phi = 0$, and

$$V_L = ec\left(\alpha \cdot \mathbf{A}\right)$$

with

$$\mathbf{A} = \frac{1}{2}\hat{\varepsilon}_L A_0 e^{ikr} e^{-i\omega t} + c.c.$$

and the corresponding amplitude of the electric field $E_0 = A_0\omega/c$ .Or

$$V_L = ecA_0 \frac{1}{2} t\left(\omega, r\right) e^{-i\omega t} + c.c.,$$

where we introduced

$$t\left(\omega, r\right) = \left(\alpha \cdot \hat{\varepsilon}_L\right) e^{ikr}.$$

This quantity may be expanded into multipole series (notice that WRJ omits the complex conjugation of the vector spherical harmonics)

$$t\left(\omega, r\right) = 4\pi \sum_{JM\lambda} i^{J-\lambda} \left(\left(\mathbf{Y}^{(\lambda)}_{JM}\left(k\right)\right)^{*} \cdot \hat{\varepsilon}_L\right) \tau^{(J\lambda)}_M$$

Here $\lambda = 0$ for magnetic and $\lambda = 1$ for electric multipoles and irreducible tensor operators $\tau^{(J\lambda)}_M$of rank J are related to the multipole operators as

$$\tau^{(J\lambda)}_M = i\left(\frac{\left(2J+1\right)\left(J+1\right)}{4\pi J}\right)^{1/2} \frac{k^J}{(2J+1)!!} q^{(J\lambda)}_M$$

Notice that the operators $q_M^{(J\lambda)}$ do not include charge! For example for E1 in atomic units and for the electron,

$$\tau_M^{(1,1)} = i\frac{k}{\sqrt{6\pi}}\mathbf{r}_M = -i\frac{k}{\sqrt{6\pi}}\mathbf{D}_M$$

Specialized expression for our geometry: z-axis along wavevector $\mathbf{k}$. Then for $\lambda = 0, 1$, the non-vanishing components are

$$\left(\mathbf{Y}_{JM}^{(\lambda)}\left(\hat{\mathbf{e}}_z\right)\right)^* = \left(\hat{\mathbf{e}}_M\right)^* \sqrt{\frac{[J]}{8\pi}} \times \begin{cases} 1, & M=-1 \\ (-1)^{\lambda+1}, & M=+1 \end{cases}$$

Further for linear polarization along the x-axis,

$$\left(\mathbf{Y}_{JM}^{(\lambda)}\left(\hat{\mathbf{e}}_z\right)\right)^* \cdot \hat{\mathbf{e}}_x = \sqrt{\frac{[J]}{16\pi}} \times \left((-1)^{\lambda}\delta_{M,1} + \delta_{M,-1}\right) \tag{9}$$

Length-form for electric multipoles

$$\langle i||q^{(J,\lambda=1)}||j\rangle = \langle \kappa_i||C_J||\kappa_j\rangle \times \int_0^\infty r^J dr\{G_iG_j + F_iF_j\}$$

Magnetic multipoles, long-wavelength approximation

$$\langle i||q^{(J,\lambda=0)}||j\rangle = \frac{\kappa_i+\kappa_j}{J+1}\langle -\kappa_i||C_J||\kappa_j\rangle \times \int_0^\infty r^J dr\{G_iF_j + F_iG_j\}$$

7.1 Matrix elements

The theory of multipole moments can be found in the WRJ book. Limit $z \to 0$ for spherical Bessel functions

$$j_n(z) \approx \frac{z^n}{(2n+1)!!}$$

Electric-multipole transitions, long-wavelength approximation.
Length-form

$$\langle i||q_J||j\rangle = \langle \kappa_i||C_J||\kappa_j\rangle \times \int_0^\infty r^J dr\{G_iG_j + F_iF_j\}.$$

Velocity-form (absorption process, $\omega > 0$)

$$\langle i||q_J||j\rangle = \frac{c}{\omega}\langle \kappa_i||C_J||\kappa_j\rangle \times \int_0^\infty r^{J-1} dr\{(\kappa_j - \kappa_i + J)G_iF_j + (\kappa_j - \kappa_i - J)F_iG_j\}.$$

Magnetic multipoles, long-wavelength approximation ($2c$ is alredy taken into account)

$$\langle i||M_J||j\rangle = 2c\frac{\kappa_i+\kappa_j}{J+1}\langle -\kappa_i||C_J||\kappa_j\rangle \times \int_0^\infty r^J dr\{G_iF_j + F_iG_j\},$$

in the non-relativistic limit

$$\langle i||M_1||j\rangle \approx -\frac{1}{2}\left(\kappa_i+\kappa_j\right)\left(\kappa_i+\kappa_j-1\right)\langle -\kappa_i||C_1||\kappa_j\rangle \int_0^\infty dr\ P_i\left(r\right)P_j\left(r\right)$$

8 Rate formulas

Transition from state $|a\rangle$ to state $|b\rangle$

$$A^{E1}_{a\to b} = \frac{4}{3}\alpha\frac{\omega^3}{c^2}\frac{S^{E1}_{ab}}{[J_a]} = 2.1410\times 10^{10}\ \left\{\omega\,(a.u.)\right\}^3\frac{S^{E1}_{ab}}{[J_a]}\,1/\mathrm{s} = \frac{2.02613\times 10^{18}}{(\lambda(\mathring{\mathrm{A}}))^3}\,\frac{S^{E1}_{ab}}{[J_a]}\,1/\mathrm{s}$$

$$S^{E1}_{ab} = |\langle a||r||b\rangle|^2$$

Here $A^{E1}_{a\to b}$ is Einstein A coefficient for spontaneous emission, S - line strength expressed in atomic units.

8.1 Black-body radiation

The average electric field radiated by a black body at temperature T

$$\langle\mathcal{E}^2\rangle = (831.9\ \mathrm{V/m})^2\left[\frac{T\,(\mathrm{K})}{300}\right]^4$$

9 Complex multi-electron atoms

9.1 Correlation Effects

1. Correlation effects decrease with Z.
2. Correlation effects decrease with n.

9.2 Coupling Schemes

9.2.1 $L-S$-coupling

For states formed from identical orbitals (e.g. $(1s)^2$) $L+S$ must be even.

9.2.2 $j-j$-coupling

For states formed from identical orbitals (e.g. $(1s)^2$) J must be even.

9.2.3 Connection between $j-j$ and $L-S$ coupling

The transformation matrix from LS states coupled to J to j_1-j_2 states coupled to J :

$$T_{LS,j_1,j_2} = \langle[(l_1,l_2)L,(s_1,s_2)S]J|[(l_1,s_1)j_1,(l_2,s_2)j_2]J\rangle = \sqrt{[L,S,j_1,j_2]}\begin{Bmatrix} l_1 & l_2 & L \\ s_1 & s_2 & S \\ j_1 & j_2 & J \end{Bmatrix}$$

9.3 Hund's rules

Allowed terms for equivalent electrons (Landau-Lifshitz v.2)

configuration	term
s^2	^1S
p, p^5	^2P
p^2, p^4	$^1SD\ \ ^3P$
p^3	$^2PD\ ^4S$
d, d^9	^2D
d^2, d^8	$^1SDG\ \ ^3PF$
d^3, d^7	$^2PDFGH\ \ ^4PF$
d^4, d^6	$^1SDFGI\ ^3PDFGH\ ^5D$
d^5	$^2SPDFGHI\ \ ^4PDFG\ ^6S$

10 Radiative corrections

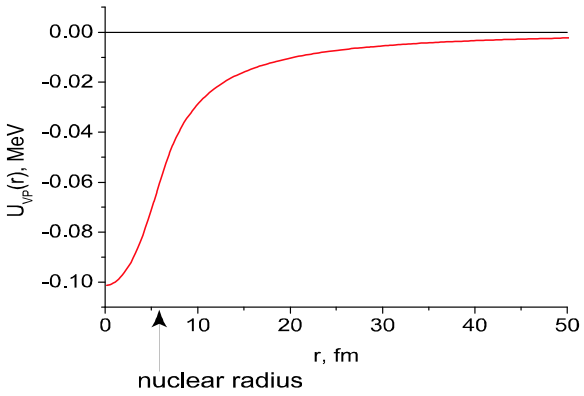
Vacuum polarization. Uehling potential for a point-like charge

$$U_{\rm VP}^{\rm p.c.}(r) = \frac{2}{3\pi}\frac{\alpha Z}{r}\int_1^\infty dt\sqrt{t^2-1}\left(\frac{1}{t^2}+\frac{1}{2t^4}\right)\exp\left[-\frac{2r}{\alpha}t\right]. \qquad (10)$$

This potential has to be folded with the nuclear charge distribution,

$$U_{\rm VP}(r) = \int d\mathbf{r}'\rho_{\rm nuc}(|\mathbf{r}-\mathbf{r}'|)U_{\rm VP}^{\rm p.c.}(r').$$

We approximated $\rho_{\rm nuc}(r)$ with the Fermi distribution. Routine from Ref. [Hni94] is useful in numerical evaluation.



11 Perturbative Approaches. General Formalisms

11.1 Textbook results (non-degenerate case, time-independent PT)

Corrections to wave-function

$$|\psi_n^{(1)}\rangle = \sum_{k\neq n} |\psi_k^{(0)}\rangle \frac{\langle\psi_k^{(0)}|V|\psi_n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}}$$

$$|\psi_n^{(2)}\rangle = \sum_{k\neq n}\sum_{l\neq n} |\psi_k^{(0)}\rangle \frac{V_{kl}\ V_{l\ n}}{\left(E_n^{(0)} - E_k^{(0)}\right)\left(E_n^{(0)} - E_l^{(0)}\right)} - \sum_{k\neq n} |\psi_k^{(0)}\rangle \frac{V_{nn}\ V_{kn}}{\left(E_n^{(0)} - E_k^{(0)}\right)^2}$$

Corrections to the energy

$$E_n^{(1)} = V_{nn}$$

$$E_n^{(2)} = \sum_{k\neq n} \frac{V_{nk}V_{kn}}{E_n^{(0)} - E_k^{(0)}}$$

$$E_n^{(3)} = \sum_{k,m\neq n} \frac{V_{nm}V_{mk}V_{kn}}{\left(E_m^{(0)} - E_n^{(0)}\right)\left(E_k^{(0)} - E_n^{(0)}\right)} - V_{nn}\sum_{m\neq n} \frac{V_{nm}V_{mn}}{\left(E_m^{(0)} - E_n^{(0)}\right)^2}$$

11.2 Dalgarno-Lewis method

Consider second-order correction to the energy

$$\delta E^{(2)} = -\sum_k \frac{\langle\Psi_0|V|\Psi_k\rangle\langle\Psi_k|V|\Psi_0\rangle}{E_k - E_0}$$

Introduce

$$|\delta\Psi\rangle = \sum_k \frac{1}{E_k - E_0}|\Psi_k\rangle\langle\Psi_k|V|\Psi_0\rangle$$

Then

$$\delta E^{(2)} = -\langle\Psi_0|V|\delta\Psi\rangle$$

Multiply by $\left(\hat{H}_0 - E_0\right)$

$$\left(\hat{H}_0 - E_0\right)|\delta\Psi\rangle = \sum_k \frac{1}{E_k - E_0}\left(\hat{H}_0 - E_0\right)|\Psi_k\rangle\langle\Psi_k|V|\Psi_0\rangle$$
$$= \sum_k |\Psi_k\rangle\langle\Psi_k|V|\Psi_0\rangle = V|\Psi_0\rangle$$

i.e. one may solve an inhomogeneous equation for the correction

$$\left(\hat{H}_0 - E_0\right)|\delta\Psi\rangle = V|\Psi_0\rangle$$

and find the correction to the energy as

$$\delta E^{(2)} = -\langle\Psi_0|V|\delta\Psi\rangle$$

11.3 Time-dependent PT

11.3.1 Interaction picture

The Hamiltonian is split into two parts $H = H_0 + V(t)$. The traditional Schrodinger state $|\psi(t)\rangle$ is transformed as

$$|\widetilde{\psi}(t)\rangle = U(t)\,|\psi(t)\rangle$$

with

$$U(t) = \exp\left(\frac{i}{\hbar}H_0 t\right)$$

The modified S.E.

$$i\hbar\frac{d}{dt}|\widetilde{\psi}(t)\rangle = \widetilde{V}(t)\,|\widetilde{\psi}(t)\rangle$$

$$\widetilde{V}(t) = U(t)\,V(t)\,U^{\dagger}(t) = \exp\left(\frac{i}{\hbar}H_0 t\right)V(t)\exp\left(-\frac{i}{\hbar}H_0 t\right)$$

The first-order probability

$$P_{s\to k}(t) = \left|-\frac{i}{\hbar}\int_{t_0}^{t} V_{ks}(t')\,e^{i\omega_{ks}t'}\,dt'\right|^2$$

11.4 Brillouin-Wigner (BW) vs. Rayleigh-Schrödinger (RS)

Advantages of BW vs RS:

1. Since the energy denominator contains $E - E_\alpha$ (E is an exact energy) instead of $E_\alpha - E_\beta$ of RS there is no blowing up terms in the case of (accidental) degeneracy.
2. The obtained matrix elements satisfy hermicity condition $\langle a|Op|b\rangle = (\langle b|Op|a\rangle)^*$, the RS, in general, does not have this important property.
3. $\pm$ Unlinked terms should disappear since they do not have correct linear dependence on the number of particles in the system.

Advantages of RS vs BW:

1. Each order of energy has the right linear dependence on the number of particles in the system, unlike BW.
2. For $\forall$ terms of RS there is a unique correspondence to diagrams.
3. No need to know the exact energy E *a priory* as in BW.

11.5 Rayleigh-Schrödinger

Non-standard 0-order approximation: *model space (P-space)* to build a perturbed w.f from degenerate(or nearly degenerate) basis. Possible criteria for inclusion in P is a ratio of the matrix element of V to the energy difference. If the ratio is large ($\rangle 1$), then the PT would diverge, so try to treat more exactly by including in P-space. Remaining functional space is labeled as Q-space (orthogonal space). Corresponding projection op.:

$$P = \sum_{\alpha \in P} |\alpha\rangle\langle\alpha| \ , \ Q = \sum_{\beta \notin P} |\beta\rangle\langle\beta|$$

Let d be the number of w.f. in the model space. Exact to model function mapping $\phi_a = P\psi_a$, $\{a = \overline{1,d}\}$, model to exact $\psi_a = \Omega\phi_a$. Ω is a *wave operator. Correlation op.* $\chi : \Omega = 1 + \chi$.
Below $\{\alpha, \alpha', \ldots\}$ span P-space, $\{\beta, \beta', \ldots\}$ - Q-space.
Useful identities:

$$\langle\alpha|\Omega|\alpha'\rangle = \delta_{\alpha,\alpha'}, \ \langle\alpha|\chi|\alpha'\rangle = 0.$$

$$\psi_i = \phi_i + \sum_\beta \langle\beta|\chi|\phi_i\rangle \cdot |\beta\rangle$$

11.5.1 Generalized Bloch Equation

$$[\Omega, H_0]P = QV\Omega P - \chi PV\Omega P$$

if the P-space is completely degenerate $\Leftarrow$ original Bloch eq.:

$$(E_0 - H_0)\Omega P = QV\Omega P - \chi PV\Omega P$$

Two approaches (power of V expansion or iterations) to perturbative solution:
1.*Order-by-order*: Find an Ω expansion in powers of V

$$\Omega = 1 + \Omega^{(1)} + \Omega^{(2)} + \ldots$$

Gives

$$[\Omega^{(n)}, H_0]P = QV\Omega^{(n-1)}P - \sum_{m=1}^{n-1} \Omega^{(n-m)}PV\Omega^{(m-1)}$$

2. *Iterative*. Start with $\Omega = 1$

$$[\Omega_{(n+1)}, H_0]P = QV\Omega_{(n)}P - \chi_{(n)}PV\Omega_{(n)}P$$

Explicitly orders-by-orders for V-powers solution:

$$\langle\beta|\Omega^{(1)}|\alpha\rangle = \frac{\langle\beta|V|\alpha\rangle}{E_0^\alpha - E_0^\beta}$$

$$\langle\beta|\Omega^{(2)}|\alpha\rangle = \sum_{\beta'} \frac{\langle\beta|V|\beta'\rangle\langle\beta'|V|\alpha\rangle}{(E_0^\alpha - E_0^\beta)(E_0^\alpha - E_0^{\beta'})} - \sum_{\alpha'} \frac{\langle\beta|V|\alpha'\rangle\langle\alpha'|V|\alpha\rangle}{(E_0^\alpha - E_0^\beta)(E_0^{\alpha'} - E_0^\beta)}$$

11.5.2 Effective Hamiltonian

The eigenvectors of the effective Hamiltonian represent the model functions, the eigenvalues are the exact energies of the exact w.f.

$$H_{\text{eff}} \equiv PH\Omega P \ , \quad H_{eff}\phi_i = E_i\phi_i$$

The practical approach is to find the $\chi^{(1)}$, build the second-order effective Hamiltonian:

$$H^{(2)}_{\text{eff}} = P(H_0 + V + V\chi^{(1)})P$$

and solve the eigenvalue problem in P-space to find the second order energies.

$$(H^{(2)}_{\text{eff}} - E^{(2)})|\alpha\rangle = 0$$

The H_{eff} is, generally, non-hermitian. The first order corrections disappear if $V = 1/r_{12} - U_{HF}$.

11.6 Brillouin-Wigner

One has to know an exact energy E in advance, this leads to a necessity to carry out the energy expansion self-consistently.

$$(H_0 + V)\psi = E\psi$$

We know the spectrum of H_0 - a set of $\{\ \phi_j, E_0^j\ \}$.
Projection operator P with respect to the reference function ϕ_0 - zero order approximation:

$$P = |\phi_0\rangle\langle\phi_0|$$

the rest of the space is spanned by Q-operator: $Q = 1 - P$.

11.6.1 Wave Function

Intermediate normalization: $\langle\phi_0|\psi\rangle = 1$. Recursion relation for the exact w.f. ψ

$$\psi = \phi_0 + T_E V\psi$$

$T_E = \frac{Q}{E-H_0}$ is a *resolvent*. The expansion is obtained by iterating the above relation.

$$\psi = (1 + \frac{Q}{E - H_0}V + \frac{Q}{E - H_0}V\frac{Q}{E - H_0}V + ...)\phi_0$$

or by orders

$$\psi^{(0)} = \phi_0,$$
$$\psi^{(1)} = \sum_{j\neq 0} \frac{|\phi_j\rangle\langle\phi_j|V|\phi_0\rangle}{E - E_0^j},$$
$$\psi^{(2)} = \sum_{j,k\neq 0} \frac{|\phi_j\rangle\langle\phi_j|V|\phi_k\rangle\langle\phi_k|V|\phi_0\rangle}{(E - E_0^j)(E - E_0^k)}$$

Also $\psi = \Omega_E\phi_0$, where *wave operator* Ω_E satisfies $\Omega_E = 1 + T_E V\Omega_E$

11.6.2 Energy Expansion

$$E = E_0 + \langle\phi_0|V\Omega_E|\phi_0\rangle$$

Def: *"Effective interaction"* $W_E = V\Omega_E$. It has the same result acting on ϕ_0 as V acting on ψ : $W_E\phi_0 = V\psi$.
n-th order of energy expansion:

$$E^{(n)} = \langle\phi_0|V\left(\frac{Q}{E-H_0}V\right)^{n-1}|\phi_0\rangle$$

or explicitly

$$E^{(1)} = \langle\phi_0|V|\phi_0\rangle,$$
$$E^{(2)} = \sum_{i\neq 0}\frac{\langle\phi_0|V|\phi_i\rangle\langle\phi_i|V|\phi_0\rangle}{E-E_0^i}$$

12 Second Quantization for Complex Atoms

12.1 Anti-commutators:

$$a_j^\dagger a_k^\dagger = -a_k^\dagger a_j^\dagger,$$
$$a_j a_k = -a_k a_j,$$
$$a_j a_k^\dagger = \delta_{jk} - a_k^\dagger a_j$$
$$a_j a_j \equiv 0$$
$$a_j^\dagger a_j^\dagger \equiv 0$$

12.2 Physical operators

One-particle operator

$$F = \sum_{kl}\langle k|f|l\rangle a_k^\dagger a_l$$

Two-particle operator

$$G = \frac{1}{2}\sum_{ijkl} g_{ijkl}a_i^\dagger a_j^\dagger a_l a_k,$$

here

$$g_{ijkl} \equiv \langle ij|g|kl\rangle \equiv \int d^3r_1 d^3r_2 \psi_i^\dagger(r_1)\psi_j^\dagger(r_2)g(r_{12})\psi_k(r_1)\psi_l(r_2)$$

Any two-particle operator B can be represented as a sum of zero-body $B^{(0)}$, one-body $B^{(1)}$ and two-body $B^{(2)}$ terms.

$$B^{(0)} = \frac{1}{2}\sum_{ab} \tilde{b}_{abab}\,,$$
$$B^{(1)} = \sum_{ij}\left(\sum_{a} \tilde{b}_{iaja}\right) : a_i^\dagger a_j :,$$
$$B^{(2)} = \frac{1}{2}\sum_{ijkl} b_{ijkl} : a_i^\dagger a_j^\dagger a_l a_k :.$$

12.3 Notation for subscripts

- a,b,c,d ...- core orbitals;
- m,n ...,r,s - excited (virtual) orbitals, including valence;
- v,w ...- valence orbitals;
- i,j...,k,l ...- any orbitals;

$$a^\dagger_{\rm core}|0_c\rangle = 0\ ,\ a_{\rm virt}|0_c\rangle = 0$$

12.4 Normal form of Operators :A:

The operators are rearranged so

$$a_{\rm core}\ and\ a^\dagger_{\rm virt}\ appear\ to\ the\ left\ of\ a^\dagger_{\rm core}\ and\ a_{\rm virt}$$

The operators in normal form give 0 when acted on core.

12.4.1 Wick's Expansion into Normal Products

$$A =: A : + : \overline{A} :$$

$: \overline{A} :$ is the sum of normal ordered terms obtained by making all possible single, double, triple ... contractions within A. Contractions are defined as $\overline{xy} \equiv xy- : xy :$.
The sign of $: A :$ is $(-1)^p$ (p is a number of permutations to bring A in normal form). Same rule holds for terms in $: \overline{A} :$ - we count permutations necessary to bring the contracted operators together + the permutations to bring the obtained term in normal form. Notice that moving a string of two operators simultaneously does not change the sign of the total string.
The only nonvanishing contractions are

$$\overline{a_m a_n^\dagger} = \delta_{mn},\ \overline{a_a^\dagger a_b} = \delta_{ab}.$$

All contractors between core and excited states vanish.

12.4.2 Wick's Theorem for Operator Products

$$: A : \cdot : B :=: AB : + : \overline{AB} :$$

Here $: \overline{AB} :$ represents the sum of the normal-ordered terms with all possible contractions between the operators in A and those in B.

12.5 Evaluation of Matrix elements in Second Quantization

12.5.1 Real Vacuum

Operators in normal form $: A :$ with respect to real vacuum:

$$\textit{All } a_i^\dagger \textit{ are on left side, all } a_k \textit{ are on the right side.}$$

Then $: A : |0\rangle = 0$, provided there is at least one a_i in A. Also $\langle 0| : A := 0$, provided there is at least one $a_i^\dagger$ in A. Using Wick's expansion in normal products (12.4.1) we see that

$$\langle 0|A|0\rangle = \text{terms w/o normal products}$$

The terms w/o normal products are those where the maximum number of contractions is achieved.

12.5.2 Quasi-vacuum $|0_c\rangle$

Rules for evaluating products $: A :: B : |0_c\rangle$
1. Several rules for evaluating $\langle 0_c|A|0_c\rangle$.
$\langle 0_c|A|0_c\rangle = 0$ if

1. the number of operators is odd.
2. the number of virtual orbitals is odd.
3. the number of core orbitals is odd.
4. the number of $a^\dagger_{virt} \neq$ the number of a_{virt}.
5. the number of $a^\dagger_{core} \neq$ the number of a_{core}

After such selection one uses the Wick's theorem. In the Wick's expansion only the terms w/o operators in normal form remain. They correspond to the maximum number of contractions in A.
Suppose we deal with a matrix element containing two normal products: $M = \langle 0_c| : A :: B : |0_c\rangle$. Then $M = 0$ unless the number of operators in $: A :$ equals that of in $: B :$. This fact immediately follows from the Wick's theorem of expansion of operator products.
When dealing with matrix elements of several operators in normal form the following observation is valuable:
$M = \langle 0_c| : A :: B :: C : |0_c\rangle$ can be obtained by calculating only contractions between $: A :$ and $: B :$ (or $: B :$ and $: C :$) having a number of operators equal to that of in $: C :$ ($: A :$).

13 Many-Body Perturbation Theory

Arrange the expansion terms according to the number of particles excited, instead of powers of V. It allows for all-order treatment of the expansion.

13.1 Atomic Hamiltonian in Normal Form

The indexing scheme is def. in **??**.

$$
\begin{aligned}
H &= H_0 + V, \\
H_0 &= E^0_{\text{core}} + \sum_k \varepsilon_k :\ a^\dagger_k a_k :, \\
V &= V_{\text{core}} + \sum_{ij} (V_{\text{HF}} - U)_{ij} :\ a^\dagger_i a_j : + \frac{1}{2} \sum_{ijkl} g_{ijkl} : a^\dagger_i a^\dagger_j a_l a_k :
\end{aligned}
$$

Here

$$
E^0_{\text{core}} = \sum_a \varepsilon_a \ ,\ V_{\text{core}} = \sum_a [\frac{1}{2} V^{\text{HF}}_{aa} - U_{aa}]
$$

and

$$
(V_{\text{HF}})_{ij} \equiv \sum_b (g_{ibjb} - g_{ibbj})
$$

13.2 Wave Operator Expansion

General expression

$$
\Omega = 1 + \sum_{ij} : a^\dagger_i a_j : \rho^i_j + \frac{1}{2} \sum_{ijkl} : a^\dagger_i a^\dagger_j a_l a_k : \rho^{ij}_{kl} + \frac{1}{3!} \sum \cdots
$$

For closed shell systems (explicit indexing)

$$
\Omega = 1 + \sum_{ar} a^\dagger_r a_a \rho^r_a + \frac{1}{2} \sum_{abrs} a^\dagger_r a^\dagger_s a_b a_a \rho^{rs}_{ab} + \cdots
$$

From PT one gets ((k) superscript is the order of V) :

$$
\begin{aligned}
\rho^{r(1)}_a &= \frac{\langle r|v|a\rangle}{\varepsilon_a - \varepsilon_r} \\
\rho^{rs(1)}_{ab} &= \frac{g_{rsab}}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}
\end{aligned}
$$

13.3 Random Phase Approximation

RPA (Random Phase Approximation) corresponds to shielding of the external applied field.

$$Z^{RPA}_{an} = z_{an} + \sum_{bm} \frac{Z^{RPA}_{bm} \tilde{g}_{amnb}}{\varepsilon_b - \varepsilon_m - \omega} + \sum_{bm} \frac{\tilde{g}_{abnm} Z^{RPA}_{mb}}{\varepsilon_b - \varepsilon_m + \omega}$$

$$Z^{RPA}_{na} = z_{na} + \sum_{bm} \frac{Z^{RPA}_{bm} \tilde{g}_{nmab}}{\varepsilon_b - \varepsilon_m - \omega} + \sum_{bm} \frac{\tilde{g}_{nbam} Z^{RPA}_{mb}}{\varepsilon_b - \varepsilon_m + \omega}$$

$$\omega = \varepsilon_w - \varepsilon_v$$

13.4 Brueckner orbitals

Brueckner orbital corrections correspond to valence electron polarizing the core. Then the valence electron gets attracted to the polarized core, reducing size of its orbit. Self-energy operator corresponds to core polarizability term in the model-potential Hamiltonian

$$\Sigma(r', r) \to \frac{\alpha_c}{2r^4} \delta(r' - r)$$

14 Angular momentum

14.1 Spherical basis vectors

$$\hat{\mathbf{e}}_x = \frac{1}{\sqrt{2}} (\hat{\mathbf{e}}_{-1} - \hat{\mathbf{e}}_{+1})$$

$$\hat{\mathbf{e}}_y = \frac{i}{\sqrt{2}} (\hat{\mathbf{e}}_{-1} + \hat{\mathbf{e}}_{+1})$$

$$\hat{\mathbf{e}}_z = \hat{\mathbf{e}}_0$$

and vice versa

$$\hat{\mathbf{e}}_{+1} = -\frac{1}{\sqrt{2}} (\hat{\mathbf{e}}_x + i\hat{\mathbf{e}}_y)$$

$$\hat{\mathbf{e}}_0 = \hat{\mathbf{e}}_z$$

$$\hat{\mathbf{e}}_{-1} = \frac{1}{\sqrt{2}} (\hat{\mathbf{e}}_x - i\hat{\mathbf{e}}_y)$$

From these definitions

$$(\mathbf{e}_\mu)^* = (-1)^\mu \, \mathbf{e}_{-\mu}$$

Notice that the scalar product (with complex conjugation)

$$(\hat{\mathbf{e}}^*_M \cdot \hat{\mathbf{e}}_{M'}) = \delta_{MM'}$$

However, the conventional scalar product does not include the complex conjugation.

14.2 Properties of angular momentum

$$
\begin{aligned}
J_+ &= J_x + iJ_y \\
J_- &= J_x - iJ_y \\
J_x &= \left(J_+ + J_-\right)/2 \\
J_y &= \left(J_+ - J_-\right)/\left(2i\right) \\
\left[J_z, J_+\right] &= +\hbar J_+ \\
\left[J_z, J_-\right] &= -\hbar J_- \\
e^{i\gamma J_z} J_+ e^{-i\gamma J_z} &= J_+ e^{i\gamma} \\
e^{i\gamma J_z} J_- e^{-i\gamma J_z} &= J_- e^{-i\gamma} \\
J^2 &= \frac{1}{2}\left(J_+ J_- + J_- J_+\right) + J_z^2
\end{aligned}
$$

Eigenvectors

$$
\begin{aligned}
J_z|JM\rangle &= M|JM\rangle \\
J_+|JM\rangle &= \left\{J\left(J+1\right) - M\left(M+1\right)\right\}^{1/2}|J, M+1\rangle \\
J_-|JM\rangle &= \left\{J\left(J+1\right) - M\left(M-1\right)\right\}^{1/2}|J, M-1\rangle \\
\langle JM'|J_+|JM\rangle &= \left\{J\left(J+1\right) - M\left(M+1\right)\right\}^{1/2}\delta_{M',M+1} \\
\langle JM'|J_-|JM\rangle &= \left\{J\left(J+1\right) - M\left(M-1\right)\right\}^{1/2}\delta_{M',M-1}
\end{aligned}
$$

14.3 nJ-symbols and Clebsh-Gordan coefficients

Properties of 3j-symbol

$$
\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \propto \Delta\left(j_1 j_2 j_3\right)\delta\left(m_1 + m_2 + m_3 = 0\right)
$$

Even number of permutations of the columns does not change the value of a 3j-symbol, while odd permutation introduces a phase factor of $(-1)^{j_1+j_2+j_3}$.

$$
\begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}
$$

Relation between CG and 3j

$$
\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_3+m_3+2j_1}\frac{1}{\sqrt{[j_3]}}C^{j_3 m_3}_{j_1 -m_1\, j_2 -m_2} \tag{11}
$$

$$
C^{j_3 m_3}_{j_1 m_1\, j_2 m_2} = (-1)^{j_1 - j_2 + m_3}\sqrt{[j_3]}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 \end{pmatrix} \tag{12}
$$

Special cases

$$\begin{pmatrix} j & 0 & j \\ -m & 0 & m \end{pmatrix} = \frac{(-1)^{j-m}}{\sqrt{[j]}} \tag{13}$$

$$(-1)^{j-m} \begin{pmatrix} j & 1 & j \\ -m & 0 & m \end{pmatrix} = \frac{1}{\{j\,(j+1)\,(2j+1)\}^{1/2}} m \tag{14}$$

$$\begin{pmatrix} j & k & j \\ -j & 0 & j \end{pmatrix} = \frac{(2j)!}{\{(2j-k)!\,(2j+k+1)!\}^{1/2}} \tag{15}$$

$$C^{00}_{j_1 m_1\, j_2 m_2} = (-1)^{j_1 - m_1}\, \delta_{j_1 j_2} \delta_{m_1, -m_2} \frac{1}{\sqrt{2j_1+1}}$$
$$C^{JM}_{j_1 m_1\, 00} = \delta_{J j_1} \delta_{m_1, M}$$

Properties of 6j-symbol The triangular conditions between the following momenta must be satisfied

$$\left\{ \begin{matrix} \bigcirc & \bigcirc & \bigcirc \\ & & \end{matrix} \right\}, \left\{ \begin{matrix} & & \bigcirc \\ \bigcirc & \bigcirc & \end{matrix} \right\}, \left\{ \begin{matrix} & \bigcirc & \\ \bigcirc & & \bigcirc \end{matrix} \right\}, \left\{ \begin{matrix} \bigcirc & & \\ & \bigcirc & \bigcirc \end{matrix} \right\}$$

Columns may be interchanged freely, and also any two numbers in the bottom row of a 6j-symbol may be interchanged with the corresponding two numbers in the top row.
One of the angular momenta is zero

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ l_1 & l_2 & 0 \end{Bmatrix} = \frac{(-1)^{j_1+j_2+j_3}}{\sqrt{[j_1, j_2]}} \delta\,(j_1, l_2)\,\delta\,(j_2, l_1)$$

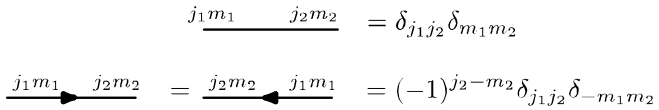
Sum rules

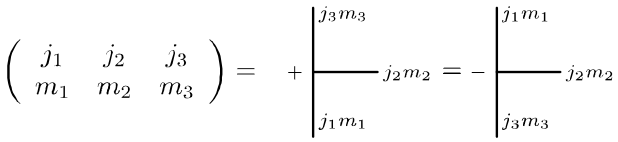
Properties of 9j-symbol

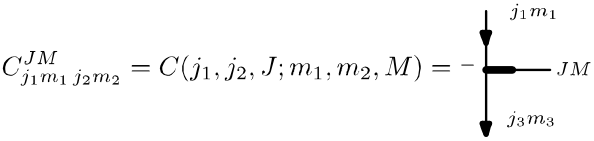
$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \\ j_7 & j_8 & j_9 \end{Bmatrix}$$

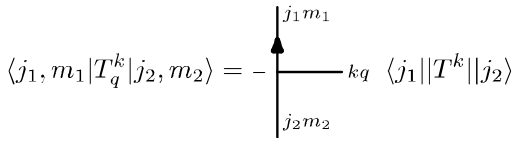
swap of any two columns or rows leads to to a phase factor $(-1)^{\sum_{k=1}^{9} j_k}$. It is invariant under reflection through one of the diagonals. The following selection rules have to be satisfied: i.e. we have triangles for each row and column of the 9j-symbol.

$$\Delta\,(j_1, j_2, j_3)\,\Delta\,(j_4, j_5, j_6)\,\Delta\,(j_7, j_8, j_9)$$
$$\Delta\,(j_1, j_4, j_7)\,\Delta\,(j_2, j_5, j_8)\,\Delta\,(j_3, j_6, j_9)$$









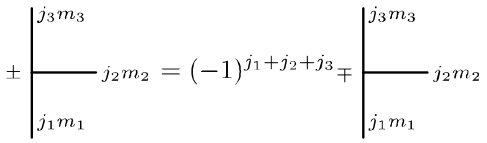
14.4 Angular momentum diagrams

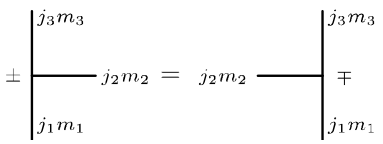
Wigner-Eckart theorem: or

$$\langle j_1, m_1 | T^k_q | j_2, m_2 \rangle = (-1)^{j_1 - m_1} \begin{pmatrix} j_1 & k & j_2 \\ -m_1 & q & m_2 \end{pmatrix} \langle j_1 || T^k || j_2 \rangle \qquad (16)$$

14.5 Transformation rules

"±" to "∓" and reverse vertex rules:





15 Spherical Tensors

Relation between extended (stretched) matrix element and reduced matrix element

$$\langle j|T_0^k|j\rangle_{\rm ext} \equiv \langle j\, m=j|T_0^k|j\, m=j\rangle = \begin{pmatrix} j & k & j \\ -j & 0 & j \end{pmatrix} \langle j||T^k||j\rangle$$

Coupling of spherical tensors: Similar to coupling of angular-momentum eigen-states

$$\left\{A^{(j_1)} \otimes\ B^{(j_2)}\right\}_{JM} = \sum_{m_1 m_2} C^{JM}_{j_1 m_1 j_2 m_2} A^{(j_1)}_{m_1} B^{(j_2)}_{m_2}$$

Recoupling formula ($M = m_1 + m_2$)

$$A^{(j_1)}_{m_1} B^{(j_2)}_{m_2} = \sum_{J=|j_1-j_2|}^{j_1+j_2} C^{JM}_{j_1 m_1 j_2 m_2} \left\{A^{(j_1)} \otimes\ B^{(j_2)}\right\}_{JM}.$$

For spherical harmonics the above formula may be simplified

$$Y_{l_1 m_1}(\theta,\phi)\, Y_{l_2 m_2}(\theta,\phi) = \frac{1}{\sqrt{4\pi}} \sum_{LM} \left(\frac{[l_1,l_2]}{[L]}\right)^{1/2} C^{L0}_{l_1 0 l_2 0} C^{LM}_{l_1 m_1 l_2 m_2} Y_{LM}(\theta,\phi) \tag{17}$$

Scalar product and rank 0 tensor

$$\left(A^{(J)} \cdot B^{(J)}\right) = \sum_{\mu} (-1)^{\mu} A^{(J)}_{\mu} B^{(J)}_{-\mu}$$

$$\left\{A^{(J)} \otimes\ B^{(J)}\right\}_{00} = \frac{(-1)^J}{\sqrt{[J]}} \left(A^{(J)} \cdot B^{(J)}\right)$$

For vectors in particular: scalar product

$$\left\{A^{(1)} \otimes\ B^{(1)}\right\}_{00} = -\frac{1}{\sqrt{3}} \left(A^{(1)} \cdot\ B^{(1)}\right)$$

vector product

$$\left\{A^{(1)} \otimes\ B^{(1)}\right\}_{1\mu} = \frac{i}{\sqrt{2}} \left[A^{(1)} \times\ B^{(1)}\right]_{\mu}$$

tensor of the second rank

$$\left\{A^{(1)} \otimes B^{(1)}\right\}_{2,+2} = A_{+1} B_{+1}$$

$$\left\{A^{(1)} \otimes B^{(1)}\right\}_{2,+1} = \frac{1}{\sqrt{2}} \left(A_{+1} B_0 + A_0 B_{+1}\right)$$

$$\left\{A^{(1)} \otimes B^{(1)}\right\}_{2,0} = \frac{1}{\sqrt{6}} \left(A_{+1} B_{-1} + 2 A_0 B_0 + A_{-1} B_{+1}\right)$$

$$\left\{A^{(1)} \otimes B^{(1)}\right\}_{2,-1} = \frac{1}{\sqrt{2}} \left(A_{-1} B_0 + A_0 B_{-1}\right)$$

$$\left\{A^{(1)} \otimes B^{(1)}\right\}_{2,-2} = A_{-1} B_{-1}$$

15.1 Reduction Theorems

Following Edmonds [Edm85].

15.1.1 Tensor product of two tensor operators

$$\langle n'J'||(T_{k_1}\otimes T_{k_2})_K||nJ\rangle = \sqrt{[K]}(-1)^{K+J+J'}\sum_{n''J''}\left\{\begin{array}{ccc} k_1 & k_2 & K \\ J & J' & J'' \end{array}\right\} \langle n'J'||T_{k_1}||n''J''\rangle\langle n''J''||T_{k_2}||nJ\rangle$$

15.1.2 Tensor product of two tensor operators acting on different subsystems

$T(k_1)$ acts on part 1 of system, $U(k_2)$ on part 2. System angular momentum JM is composed from j_1m_1 of part 1 and j_2m_2 of part 2.

$$\langle n_1'j_1'n_2'j_2'J'||(T_{k_1}\otimes U_{k_2})_K||n_1j_1n_2j_2J\rangle = \sqrt{[J,J',K]}\left\{\begin{array}{ccc} j_1' & j_1 & k_1 \\ j_2' & j_2 & k_2 \\ J' & J & K \end{array}\right\} \langle n_1'j_1'||T_{k_1}||n_1j_1\rangle\langle n_2'j_2'||U_{k_2}||n_2j_2\rangle$$

For scalar product

$$\langle(\gamma_1j_1\gamma_2j_2)\,JM||T_k\cdot U_k||\,(\gamma_1'j_1'\gamma_2'j_2')\,J'M'\rangle = (-1)^{j_1'+j_2+J}\,\delta_{JJ'}\delta_{MM'}\left\{\begin{array}{ccc} j_1 & j_1' & k \\ j_2' & j_2 & J \end{array}\right\} \langle\gamma_1j_1||T_k||\gamma_1'j_1'\rangle\langle\gamma_2j_2||U_k||\gamma_2'j_2'\rangle$$

15.1.3 Tensor operators acting on subsystem 1

$$\langle n_1'j_1'n_2'j_2'J'||T_k||n_1j_1n_2j_2J\rangle = (-1)^{j_1'+j_2+J+k}\,\sqrt{[J,J']}\left\{\begin{array}{ccc} j_1' & J' & j_2 \\ J & j_1 & k \end{array}\right\} \langle n'j_1'||T_k||nj_1\rangle\delta_{n_2n_2'}\delta_{j_2j_2'}$$

$$\langle n_aj_{a1}j_{a2}J_a||T_k||n_bj_{b1}j_{b2}J_b\rangle = (-1)^{j_{a1}+j_{b2}+J_b+k}\,\sqrt{[J_a,J_b]}\left\{\begin{array}{ccc} j_{a1} & J_a & j_{b2} \\ J_b & j_{b1} & k \end{array}\right\} \langle n_aj_{a1}||T_k||n_bj_{b1}\rangle$$

In particular, for the electric-dipole operator

$$\left|\langle n's_{1/2}||D||np_{1/2}\rangle\right| = \sqrt{\frac{2}{3}}\,|\langle n's||D||np\rangle|$$

$$\left|\langle n's_{1/2}||D||np_{1/2}\rangle\right| = \sqrt{\frac{4}{3}}\,|\langle n's||D||np\rangle|$$

15.2 Various Reduced Matrix Elements

An excellent collection of matrix elements is compiled by Varshalovich *et al.* [VMK88].
Angular momentum operator:

$$\langle j_1||J||j_2\rangle = \delta_{j_1 j_2}\sqrt{j_1(j_1+1)(2j_1+1)}$$

Normalized spherical harmonic C_q^k is defined as

$$\begin{aligned} C_q^k &= \sqrt{\frac{4\pi}{2k+1}}\, Y_{kq}(\hat{r}), \\ C_0^0 &\equiv 1, \\ C_\mu^1(\hat{r}) &= \hat{r}_\mu, \end{aligned}$$

and

$$\langle l_1||C^k||l_2\rangle = (-1)^{l_1}\sqrt{[l_1][l_2]}\begin{pmatrix} l_1 & k & l_2 \\ 0 & 0 & 0 \end{pmatrix}.$$

Symmetry property:

$$\langle l_a||C^k||l_b\rangle = (-1)^{l_a-l_b}\langle l_b||C^k||l_a\rangle.$$

For states coupled to a given j :

$$\langle \kappa_a||C^k||\kappa_b\rangle = (-1)^{j_a+1/2}\sqrt{[j_a][j_b]}\begin{pmatrix} j_a & j_b & k \\ -1/2 & 1/2 & 0 \end{pmatrix}\Pi(l_a+k+l_b),$$

where $\Pi(l)=1$ for even l, and $\Pi(l)=0$ for odd l.
Symmetry property

$$\langle \kappa_a||C^k||\kappa_b\rangle = (-1)^{j_a-j_b}\langle \kappa_b||C^k||\kappa_a\rangle.$$

Special cases:

$$\begin{aligned} \langle j'||C^0||j\rangle &= \delta_{jj'}\sqrt{[j]} \\ \langle l'||C^0||l\rangle &= \delta_{ll'}\sqrt{[l]} \\ \langle j_a||C^k||s_{1/2}\rangle &= \delta_{k,l_a}\,(-1)^{j_a+l_a-1/2}\sqrt{[j_a]/[l_a]} \end{aligned}$$

Matrix element of a unit vector $\hat{n}$ (rank 1) :

$$\langle l'||\hat{n}||l\rangle = \sqrt{[l]}(-1)^{(l-1)}\begin{pmatrix} l & l' & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

∇_Ω (rank 1):

$$\langle l'||\nabla_\Omega||l\rangle = -\{l\sqrt{l+1}\,\delta_{l'l+1} + (l+1)\sqrt{l}\,\delta_{l'l-1}\}$$

σ (rank 1):

$$\begin{aligned} \langle 1/2||\sigma||1/2\rangle &= \sqrt{6} \\ \langle\, j_a||\sigma||j_b\rangle &= \delta_{l_a l_b}(-1)^{l_a+j_a-1/2}\sqrt{[j_a,j_b]}\begin{Bmatrix} 1 & j_a & j_b \\ l_a & 1/2 & 1/2 \end{Bmatrix}\sqrt{6} \end{aligned}$$

15.3 LS-coupling

$$\langle n(LS)_J||S||n'\left(L'S'\right)_{J'}\rangle = (-1)^{S+L'+J'+1}\sqrt{[J,J']}\sqrt{S(S+1)(2S+1)}\left\{\begin{array}{ccc} S & J & L' \\ J' & S & 1 \end{array}\right\}\delta_{SS'}$$

15.4 Spherical harmonics

$$Y^*_{lm}\left(\theta,\phi\right) = Y_{lm}\left(\theta,-\phi\right) = (-1)^m Y_{l,-m}\left(\theta,\phi\right)$$

Normalized spherical harmonics $C^k_q(\hat{r})$ are defined as

$$\begin{aligned} C^k_q(\hat{r}) &= \sqrt{\frac{4\pi}{2k+1}}\, Y_{kq}(\hat{r}), \\ C^0_0 &\equiv 1 \\ C^1_\mu\left(\hat{r}\right) &= \hat{r}_\mu \end{aligned}$$

$$\delta\left(\mathbf{n}-\mathbf{n}'\right) = \delta\left(\phi-\phi'\right)\,\delta\left(\cos\theta-\cos\theta'\right) = \sum_{lm} Y^*_{lm}\left(\mathbf{n}\right) Y_{lm}\left(\mathbf{n}'\right)$$

$$Y_{l_1m_1}\left(\theta,\phi\right) Y_{l_2m_2}\left(\theta,\phi\right) = \frac{1}{\sqrt{4\pi}}\sum_{LM}\left(\frac{[l_1,l_2]}{[L]}\right)^{1/2} C^{L0}_{l_10l_20} C^{LM}_{l_1m_1l_2m_2} Y_{LM}\left(\theta,\phi\right) \tag{18}$$

15.5 Vector spherical harmonics

$$\begin{aligned} \mathbf{Y}^{(-1)}_{JM}\left(\theta,\phi\right) &= \hat{\mathbf{r}} Y_{JM}\left(\theta,\phi\right) \\ \mathbf{Y}^{(0)}_{JM}\left(\theta,\phi\right) &= \frac{1}{\sqrt{J\left(J+1\right)}}\mathbf{L} Y_{JM}\left(\theta,\phi\right) \\ \mathbf{Y}^{(+1)}_{JM}\left(\theta,\phi\right) &= \frac{r}{\sqrt{J\left(J+1\right)}}\nabla Y_{JM}\left(\theta,\phi\right) = -i\left[\hat{\mathbf{r}}, \mathbf{Y}^{(0)}_{JM}\left(\theta,\phi\right)\right] \end{aligned}$$

Normalized harmonics

$$\mathbf{C}^{(\lambda)}_{kq} = \sqrt{\frac{4\pi}{2k+1}}\,\mathbf{Y}^{(\lambda)}_{kq}(\hat{r})$$

Apparently

$$\hat{\mathbf{r}} = (4\pi)^{1/2}\,\mathbf{Y}^{(-1)}_{00}\left(\hat{\mathbf{r}}\right) = \mathbf{C}^{(-1)}_{00}$$

Matrix elements of normalized vector spherical harmonics times σ :

$$\begin{aligned} \langle\kappa_b m_b|\sigma\cdot\mathbf{C}^{(-1)}_{kq}|\kappa_a m_a\rangle &= -\langle -\kappa_b m_b|\, C^k_q|\,\kappa_a m_a\rangle \\ \langle\kappa_b m_b|\,\sigma\cdot\mathbf{C}^{(0)}_{kq}|\,\kappa_a m_a\rangle &= \frac{\kappa_a-\kappa_b}{\sqrt{k(k+1)}}\langle\kappa_b m_b|\, C^k_q|\,\kappa_a m_a\rangle \\ \langle\kappa_b m_b|\,\sigma\cdot\mathbf{C}^{(1)}_{kq}|\,\kappa_a m_a\rangle &= \frac{\kappa_a+\kappa_b}{\sqrt{k(k+1)}}\langle -\kappa_b m_b|\, C^k_q|\,\kappa_a m_a\rangle \end{aligned}$$

16 Rotations

16.1 Wigner D-functions

The wave-function in the initial (θ, ϕ) and the rotated (θ', ϕ') frames are related as

$$\Psi_{JM'}(\theta', \phi', \sigma') = \sum_{M=-J}^{J} \Psi_{JM}(\theta, \phi, \sigma)\ D^J_{MM'}(\alpha, \beta, \gamma)$$

$$\Psi_{JM}(\theta, \phi, \sigma) = \sum_{M=-J}^{J} \left[D^J_{MM'}(\alpha, \beta, \gamma)\right]^* \Psi_{JM'}(\theta', \phi', \sigma')$$

where α, β, γ are the Eurler angles of the rotation. Spherical tensors transform in the same way

$$T^{(J)}_{M'}(\theta', \phi', \sigma') = \sum_{M=-J}^{J} T^{(J)}_{M}(\theta, \phi, \sigma)\ D^J_{MM'}(\alpha, \beta, \gamma)$$

$$\left[D^J_{M\Omega}(\alpha, \beta, \gamma)\right]^* = D^J_{M\Omega}(-\gamma, \beta, -\alpha) = (-1)^{M-\Omega} D^J_{-M-\Omega}(\alpha, \beta, \gamma)$$

$$C_{lm}(\theta, \phi) = D^l_{0,-m}(0, \theta, \phi)$$

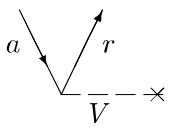
$$\delta(\mathbf{n} - \mathbf{n}') = \delta(\phi - \phi')\ \delta(\cos\theta - \cos\theta') = \sum_{lm} Y^*_{lm}(\mathbf{n})\, Y_{lm}(\mathbf{n}')$$

$$Y_{l_1 m_1}(\theta, \phi)\, Y_{l_2 m_2}(\theta, \phi) = \frac{1}{\sqrt{4\pi}} \sum_{LM} \left(\frac{[l_1, l_2]}{[L]}\right)^{1/2} C^{L0}_{l_1 0 l_2 0} C^{LM}_{l_1 m_1 l_2 m_2} Y_{LM}(\theta, \phi) \tag{19}$$

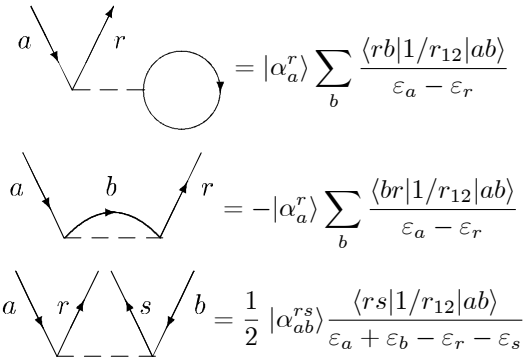
17 Goldstone Diagrams

Rules:

1. Interaction - dotted horizontal line with vertex.
2. Particle (excited orbital) - arrow up (positive time)
   Hole (core state) arrow down (negative time)
3. Initial state - incoming arrow, final state - outgoing arrow , matrix element $\langle f|V|i\rangle$.



$$= |\alpha^r_a\rangle \frac{\langle r|V|a\rangle}{\varepsilon_a - \varepsilon_r}$$



$$= |\alpha_a^r\rangle \sum_b \frac{\langle rb|1/r_{12}|ab\rangle}{\varepsilon_a - \varepsilon_r}$$

$$= -|\alpha_a^r\rangle \sum_b \frac{\langle br|1/r_{12}|ab\rangle}{\varepsilon_a - \varepsilon_r}$$

$$= \frac{1}{2}\,|\alpha_{ab}^{rs}\rangle \frac{\langle rs|1/r_{12}|ab\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

18 Numerics

18.1 B-Splines

Advantage is that a set is finite, reasonably complete, and the continuum spectrum is mocked up to be discreet.

Properties: B-spline $B_{i,k}(r)$ number i of order k is a piecewise polynomial of degree $k-1$ inside $t_i \leq r \ < t_{i+k}$. It vanishes outside this interval.

$$B_{i,k}(r) \neq 0,\ t_i \leq r \ < t_{i+k}$$

Supporting grid $\{t_j\}$ is defined as

$$t_1 = t_2 = \cdots = t_k = 0$$
$$t_n = t_{n+1} = \cdots = t_{n+k} = R$$

19 Molecules

19.1 Classification of molecular levels for diatomics

19.1.1 Zoology of various angular momenta

$\hat{\mathbf{n}}$ is the unit vector along the internuclear axis

1. Electronic orbital momentum $\mathbf{L}$, projection $\Lambda = \mathbf{L} \cdot \hat{\mathbf{n}}$.
2. Spin S, projection $\Sigma = \mathbf{S} \cdot \hat{\mathbf{n}}$.
3. Total electronic momentum $\mathbf{J}_e = \mathbf{L} + \mathbf{S}$, projection $\Omega = (\mathbf{L} + \mathbf{S}) \cdot \hat{\mathbf{n}}$.
4. Mechanical rotation of the molecule as a whole, $\mathbf{R}$. Notice that by definition $\mathbf{R} \cdot \hat{\mathbf{n}} = 0$
5. Total nuclear spin $\mathbf{T} = \mathbf{I}_1 + \mathbf{I}_2$

6. Total molecular momentum $\mathbf{J}$, notice projection on the nuclear axis

$$\mathbf{J} = ((\mathbf{L}+\mathbf{S})\cdot\hat{\mathbf{n}})\,\hat{\mathbf{n}} + \mathbf{R} = \ \Omega\hat{\mathbf{n}} + \mathbf{R}$$

   Due to the angular momenta addition rules, $J \geq \Omega$

7. "Spinless" total ang. momentum $\mathbf{K} = \mathbf{L} + \mathbf{R} = \mathbf{J} - \mathbf{S}$.

8. "Super"-total momentum $\mathbf{F} = \mathbf{J} + \mathbf{T}$

Hund's case (a). Relativistic effects are small, Λ is a projection of $\mathbf{L}$ onto the molecular axis, Σ is the projection of spin $\mathbf{S}$, $\Omega = |\Lambda + \Sigma|$. Term symbol (notice multiplicity based on S,not Σ)

$$^{2S+1}\Lambda_{\Omega}$$

Electronic energy of the multiplet

$$T_e = T_0 + A\Lambda\Sigma$$

19.1.2 Eigenstates:

Hund's case (a).

$$|JM_J\Omega\varepsilon\rangle = \frac{1}{\sqrt{2}}\left(|JM_J;\Omega\rangle\,|\Lambda,\Sigma\rangle + \varepsilon\,|JM_J;-\Omega\rangle\,|-\Lambda,-\Sigma\rangle\right)$$

where the rotational part [LBF86, Miz75]

$$|JM_J;\Omega\rangle = \left[\frac{(2J+1)}{8\pi^2}\right]^{1/2} D^J_{\Omega M_J}\ \ (\phi,\theta,\chi)$$

and $\varepsilon = \pm 1$ denote parity of the states (Wang transformations). The Wigner functions (same as in Edmonds)

$$D^J_{\Omega M_J}\ \ (\alpha,\theta,\phi)$$

are simultaneous eigenstates of J^2 , lab-frame J_z (eigenvalue M_J) and J_z in the rotating body-frame (eigenvalue Ω). Useful formula for computing matrix elements

$$\frac{1}{8\pi^2}\int d\omega D^{(j_1)}_{m_1'm_1}(\omega)\,D^{(j_2)}_{m_2'm_2}(\omega)\,D^{(j_3)}_{m_3'm_3}(\omega) = \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1' & m_2' & m_3' \end{pmatrix}$$

$$\int d\omega = \int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta\ d\beta \int_0^{2\pi} d\gamma$$

Using this formula and the transformation of the spherical tensor into the body frame,

$$T^{(J)}_{M'}(\theta',\phi',\sigma') = \sum_{M=-J}^{J} T^{(J)}_{M}(\theta,\phi,\sigma)\ \ D^J_{MM'}(\alpha,\beta,\gamma)$$

and

$$\left[D^J_{M\Omega}(\alpha,\beta,\gamma)\right]^* = (-1)^{M-\Omega} D^J_{-M-\Omega}(\alpha,\beta,\gamma)$$

we relate the matrix element in the lab frame with the mel in the body frame

$$\langle J'M'_J;\Omega'|\,T^{(k)}_{q'}\,|JM_J;\Omega\rangle^{(\text{lab})} = (-1)^{\Omega'-M'_J}\sqrt{[J]\,[J']}\sum_q \langle\Omega'|\,T^{(k)}_q\,|\Omega\rangle^{(\text{body})} \quad \times$$

$$\begin{pmatrix} J' & k & J \\ -\Omega' & q & \Omega \end{pmatrix}\begin{pmatrix} J' & k & J \\ -M'_J & q' & M_J \end{pmatrix}$$

19.1.3 Symmetries:

gerade/ungerade etc ...

Symmetric Top

The moments of intertia perpendicular to the internuclear axis $I_B = \mu R_e^2$ are much larger than I_A about the axis. The exact energy levels

$$F(J) = BJ(J+1) + (A-B)\Lambda^2$$

$$A = \frac{h}{8\pi^2 c I_A},\ B = \frac{h}{8\pi^2 c I_B}$$

19.2 Transformation from the laboratory to body-fixed frame

F is the super-total angular momentum

$$\Phi^{F,M_F}_{\text{lab}} = \sum_{K_F}\left\{\left[\frac{(2F+1)}{8\pi^2}\right]^{1/2} D^{*F}_{M_F K_F}(\phi,\theta,\chi)\right\}\Phi^{F,K_F}_{\text{body}}$$

$$T^{\text{lab}}_p = \sum_q D^{*L}_{pq}(\phi,\theta,\chi)\,T^{\text{body}}_q$$

The spherical angles ϕ and θ correspond to the Eurleur angles α are β of the body frame with respect to the lab frame.

19.3 Zeeman effect

First-order energy correction

$$E^{(1)}_B = -\bar{\mu}B$$

Here $\bar{\mu}$ is the expectaion value of the molecular magnetic moment in the direction of the field. Unless the molecule is in $^1\Sigma$ state, the magnetic moment is dominated by that due to electron (i.e. nuclear magnetic moment and rotation of the molecule as the whole may be disregarded ($\mu_B/\mu_n \sim 1/2000$)).

Case (a), M is the projection of the total angular momentum $\mathbf{J}$ on the B-field

$$\bar{\mu} = \frac{(\Lambda+2\Sigma)(\Lambda+\Sigma)}{J(J+1)} M\ \mu_B$$

Footnote: for $^2\Pi_{1/2}$, $\Lambda + 2\Sigma = 0$, and $\bar{\mu} = 0$.

19.4 Stark effect

Linear Stark effect arises if the molecular state has the electric dipole moment D, then disregarding Λ-doubling,

$$E_{\mathcal{E}}^{(1)} = -\bar{D}\ \mathcal{E}$$

where

$$\bar{D} = \frac{\Omega}{J\left(J+1\right)} M\ D$$

19.5 Long-range interactions of molecules

According to Ref. [Arr81], if two space-fixed parallel coordinate frames are introduced in the molecules A and B, their centers being at a and b, and $\mathbf{R}$ points from a to b

$$V\left(R\right) = \sum_{L_a=0} \sum_{L_b=0} \frac{V_{L_a L_b}}{R^{L_a+L_b+1}}$$

where

$$V_{L_a L_b} = \frac{\left(4\pi\right)^{1/2} \left(-1\right)^{L_b}}{\sqrt{\left[L\right]}} \left(\begin{array}{c} 2L \\ 2L_a \end{array} \right)^{1/2} \sum_{M=-L}^{L} \left(-1\right)^M Y_L^{-M} \left(\hat{R}\right) \left[\mathcal{T}_{L_a}\left(\mathbf{r}_a\right) \otimes \mathcal{T}_{L_b}\left(\mathbf{r}_b\right)\right]_M^L$$

with $L = L_a + L_b$ and

$$\mathcal{T}_L^M\left(\mathbf{r}\right) = r^L C_L^M\left(\hat{r}\right)$$

and

$$\left[\mathcal{T}_{L_a}\left(\mathbf{r}_a\right) \otimes \mathcal{T}_{L_b}\left(\mathbf{r}_b\right)\right]_M^L = \sum_{M_a M_b} \langle L_a M_a; L_b M_b | L M \rangle \mathcal{T}_{L_a}^{M_a}\left(\mathbf{r}_a\right) \mathcal{T}_{L_b}^{M_b}\left(\mathbf{r}_b\right)$$

For two parallel reference frames with z-axis fixed along $\mathbf{R}$

$$V_{L_a L_b} = \sum_{M=-L_<}^{L_<} W_{L_a L_b}^M \mathcal{T}_{L_a}^M\left(\mathbf{r}_a\right) \mathcal{T}_{L_b}^{-M}\left(\mathbf{r}_b\right)$$

$$W_{L_a L_b}^M = \frac{\left(-1\right)^{L_b} \left(L_a + L_b\right)!}{\left\{\left(L_a - M\right)! \left(L_a + M\right)! \left(L_b - M\right)! \left(L_b + M\right)!\right\}^{1/2}}$$

with $L_< = \min\left(L_a, L_b\right)$. In particular

$$V_{dd} = -\frac{1}{R^3} \sum_{\mu} w_\mu^{(1)} D_\mu^{(1)}(\mathrm{I}) D_{-\mu}^{(1)}(\mathrm{II})$$

with $w_\mu = 1 + \delta_{\mu,0}$ and the dipole operator

$$D_\mu^{(1)} = -\left|e\right| \sum_i r_i\ C_\mu^{(1)}\left(\hat{\mathbf{r}}_i\right)$$

$$V_{QQ} = \sum_{\mu=-2}^{\mu} \frac{4!}{(2-\mu)!(2+\mu)!} Q_{\mu}^{(2)}(\mathrm{I}) Q_{-\mu}^{(2)}(\mathrm{II})\,, \tag{20}$$

with quadrupole moment tensor $Q_{\mu}^{(2)}$ defined as

$$Q_{\mu}^{(2)} = -|e| \sum_i r_i^2 C_{\mu}^{(2)}(\hat{\mathbf{r}}_i)$$

The double-atom basis. For homonuclear molecules the symmetry-adapted basis formed from atomic states centered at the nuclei I and II

$$\left|\Phi_{\alpha\beta}^{p}\right\rangle = \begin{cases} \frac{1}{\sqrt{2}} \left(|\alpha\rangle_I |\beta\rangle_{II} + (-1)^p |\beta\rangle_I |\alpha\rangle_{II}\right) & \alpha \neq \beta \\ |\alpha\rangle_I |\alpha\rangle_{II} & \alpha = \beta, p = g \end{cases}$$

The completeness relation

$$1 = \sum_{(\alpha>\beta),p} \left|\Phi_{\alpha\beta}^{p}\right\rangle \left\langle\Phi_{\alpha\beta}^{p}\right| + \sum_{\alpha} |\Phi_{\alpha\alpha}^{g}\rangle \langle\Phi_{\alpha\alpha}^{g}|\,.$$

Useful Casimir-Polder identity

$$\frac{1}{a+b} = \frac{2}{\pi} \int_0^{\infty} d\omega \, \frac{a}{a^2+\omega^2} \frac{b}{b^2+\omega^2};\ a>0,\, b>0$$

Higher multipole dispersion coefficients for two spherically-symmetric atoms

From [SC85]

$$\begin{aligned} C_6 &= C_{AB}\,(1,1) \\ C_8 &= C_{AB}\,(1,2) + C_{AB}(2,1) \\ C_{10} &= C_{AB}\,(2,2) + C_{AB}\,(1,3) + C_{AB}(3,1) \end{aligned}$$

with

$$C_{AB}\,(l_1,l_2) = \frac{(2l_1+2l_2)!}{4\,(2l_1)!\,(2l_2)!} \left(\frac{2}{\pi}\right) \int_0^{\infty} \alpha_{l_1}^{A}\,(i\omega)\,\alpha_{l_2}^{B}\,(i\omega)\,d\omega$$

e.g.

$$\begin{aligned} C_{AB}\,(1,1) &= \frac{3}{\pi} \int_0^{\infty} \alpha_1^{A}\,(i\omega)\,\alpha_1^{B}\,(i\omega)\,d\omega \\ C_{AB}\,(1,2) &= \frac{15}{2\pi} \int_0^{\infty} \alpha_1^{A}\,(i\omega)\,\alpha_2^{B}\,(i\omega)\,d\omega \\ C_{AB}\,(2,2) &= \frac{35}{\pi} \int_0^{\infty} \alpha_2^{A}\,(i\omega)\,\alpha_2^{B}\,(i\omega)\,d\omega \\ C_{AB}\,(1,3) &= \frac{14}{\pi} \int_0^{\infty} \alpha_1^{A}\,(i\omega)\,\alpha_3^{B}\,(i\omega)\,d\omega \end{aligned}$$

20 Applications

20.1 EM moments

Dipole moment of the system

$$\mathbf{D} = \sum q_i \mathbf{r}_i = -|e| \sum \mathbf{r}_i$$

Interaction with the electric field

$$V = -\mathbf{D} \cdot \mathcal{E}$$

The Hamiltonian of interaction of a magnetic dipole μ with a static uniform magnetic field B is given by

$$H = -\mu \cdot \mathbf{B}$$

Magnetic moment nonrelativistically may be expressed as

$$\mu = -\mu_B \left(L + g_e S \right),$$

where the Bohr magneton is

$$\mu_B = \frac{|e| \hbar}{2m},$$

and gyromagnetic ratio for electron $g_e \approx 2.002$.

In a magnetic field, the energy levels are given by

$$E_{M_J} = \mu_B g_J B M_J \,, \tag{21}$$

where mu_B is the Bohr magneton, g_L is the Lande factor, and M is the projection of the angular momentum along the B-field. For an atom in a state $^{2S+1}L_J$, the Lange factor is given by

$$g_J = \frac{\langle nJ| \left|(J+S)\right| |nJ\rangle}{\sqrt{J}\,\sqrt{1+J}\,\sqrt{1+2\,J}} = 1 + \frac{J\,(J+1) - L\;(L+1) + S\,(S+1)}{2\,J\;(J+1)}$$

For ground state of alkali-metal atoms $g_J\left(^2S_{1/2}\right) = 2$.

For a hyperfine state, the Zeeman effect in a weak field (when the Zeeman corrections are much smaller than the HFS splitting between the energy levels) {See HAKEN, WOLF, Atomic and Quantum Physics, Springer, Berlin }

$$E_{M_F} = \mu_B g_F B M_F \,, \tag{22}$$

with the modified Lande factor

$$g_F = g_J \frac{F\,(F+1) + J\;(J+1) - I\,(I+1)}{2\,F\;(F+1)} + \\ - g_I \frac{\mu_N}{\mu_B} \frac{F\,(F+1) + I\,(I+1) - J\,(J+1)}{2\,F\;(F+1)}$$

The second contribution (nuclear moment) is about 2,000 times smaller since $\mu_N/\mu_B = m_e/m_p$.

Disregarding this term we obtain for $J = 1/2$

$$g_{F=I+1/2} = g_J \frac{1}{2I+1}$$
$$g_{F=I-1/2} = -g_J \frac{1}{2I+1}$$

i.e. for the lower HFS state the g-factor is negative.

20.2 Cooling and trapping

20.2.1 Optical lattices

In a lattice, the electric field is formed by two counter-propagating waves (original laser and the reflected wave, which is then absorbed? on the other, laser, end, so there is only one reflection)

$$E(z,t) = E_0 \cos(\omega t - kz) + E_0 \cos(\omega t + kz) = 2E_0 \cos kz \ \cos \omega t$$

we see that the effective field strength is $2E_0$. It means that given a formula for a single laser, we can upgrade to the lattice by multiplying E_0 by 2. Or intensity/power by a factor of 4.

1D-lattice potential for far-off resonance trap

$$V(r,z) = 4V_{\max} \exp\left\{-2r^2/w(z)^2\right\} \cos^2(2\pi z/\lambda)$$
$$V_{\max} = \frac{\alpha(\omega)}{c\varepsilon_0 \pi w(z)^2} P = \frac{4\pi}{c} \alpha(\omega) I,$$

where P is the laser power and $w(z)$ is the radius of the laser beam.

Lamb-Dicke regime: the spacing of vibrational levels exceeds the photon recoil energy

$$\hbar\omega_{ho} \gg E_R = \frac{(\hbar k)^2}{2M}$$

20.2.2 Static polarizabilities

Polarizability is defined as

$$\langle D_z \rangle = \alpha \mathcal{E}_z$$

(alternative definition through second order energy correction $\delta E_n = -1/2\, \alpha\, \mathcal{E}_z^2$).

For non-polar gasses (Clausius-Mossotti equation see Section 4.5 of Ref.[Jac99])

$$\alpha = \frac{3}{n} \left(\frac{\varepsilon/\varepsilon_0 - 1}{\varepsilon/\varepsilon_0 + 2} \right)$$

where ε is dielectric constant and n is the number density. The zz component of the polarizability tensor for the state ψ_s is

$$\alpha_{zz} = 2\sum_k \frac{\langle\psi_s|D_z|\psi_k\rangle\langle\psi_k|D_z|\psi_s\rangle}{E_k - E_s}$$

This tensor may be decomposed into the scalar and tensor (rank 2) parts

$$\begin{aligned}
\alpha_{zz} &= \alpha_{zz}^{(0)} + \alpha_{zz}^{(2)} \\
\alpha_{zz}^{(0)} &= \frac{2}{3}\sum_k \frac{\langle\psi_s|\mathbf{D}|\psi_k\rangle\cdot\langle\psi_k|\mathbf{D}|\psi_s\rangle}{E_k - E_s} \\
\alpha_{zz}^{(2)} &= \frac{2}{3}\sum_k \sum_{\lambda=0,\pm1} (1+\delta_{\lambda,0}) \frac{\langle\psi_s|D_\lambda|\psi_k\rangle\langle\psi_k|D_{-\lambda}|\psi_s\rangle}{E_k - E_s}
\end{aligned}$$

$$\alpha_a^{E1}(\omega) = 2\sum_b \frac{E_b - E_a}{(E_b - E_a)^2 - \omega^2} |\langle\psi_a|D_z|\psi_b\rangle|^2$$

For ground states of alkali-metals ${}^2S_{1/2}$

$$\alpha_g^{E1}\left({}^2S_{1/2},\omega\right) = \frac{1}{3}\sum_e \frac{E_e - E_g}{(E_e - E_g)^2 - \omega^2} |\langle\psi_g||D||\psi_e\rangle|^2$$

20.3 Nuclear distributions

20.3.1 Fermi-type distribution

c-nuclear radius cutoff

$$\rho(r) = \frac{\rho_0}{1 + \exp\left[(r-c)/a\right]},$$

where normalization constant ρ_0 is found from

$$\int_0^\infty 4\pi r^2 \rho(r) dr = 1.$$

A typical value of a =fm.

Moments of Fermi distribution

$$F_n(c,a) = \int_0^\infty r^n \frac{1}{1 + e^{((r-c)/a)}} dr = \; a^{n+1} I_n\left(\frac{c}{a}\right)$$

with

$$\begin{aligned}
I_n(\mu) &= \int_0^\infty x^n \frac{1}{e^{x-\mu}+1} dx = \left(\int_0^\mu + \int_\mu^\infty\right) \frac{x^n}{e^{x-\mu}+1} dx = \\
&= \int_0^\mu \frac{x^n}{e^{x-\mu}+1} dx + \int_0^\infty \frac{(y+\mu)^n}{1+e^y} dy.
\end{aligned}$$

The integrals may be expressed in terms of polylogarithms $\mathrm{Li}_n(z)$

$$\mathrm{Li}_n(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^n}. \tag{23}$$

and Rieman ζ-function. Particular values

$$\begin{aligned}
I_2(\mu) &= \frac{\pi^2}{3}\mu + \frac{1}{3}\mu^3 - 2\,\mathrm{Li}_3(-e^{-\mu}),\\
I_3(\mu) &= \frac{7\,\pi^4}{60} + \frac{\pi^2}{2}\mu^2 + \frac{1}{4}\mu^4 + 6\ \mathrm{Li}_4(-e^{-\mu}),\\
I_4(\mu) &= \frac{7\,\pi^4}{15}\mu + \frac{2\,\pi^2}{3}\mu^3 + \frac{1}{5}\mu^5 - 24\,\mathrm{Li}_5(-e^{-\mu}).
\end{aligned}$$

In terms of these integrals, the normalization factor is given by

$$\rho_0 = \frac{1}{4\pi}\left[F_2(c,a)\right]^{-1}.$$

20.3.2 Uniform distribution

$$\rho(r) = \frac{3}{4\pi R^3}\begin{cases} 1, & r \le R \\ 0, & r > R \end{cases}$$

Here the nuclear radius R is related to the r.m.s value as

$$R = \sqrt{\frac{5}{3}}\langle r^2\rangle^{1/2}$$

Fitting formula from [JS85], $A > 9$

$$\langle r^2\rangle^{1/2} = 0.836A^{1/3} + 0.570\,(\pm 0.05)\ \text{fm}.$$

20.3.3 Woods - Saxon potential for nucleons

$$\begin{aligned}
V_{\mathrm{WS}} &= V_0 f(r) + V_{ls}\ (l\cdot s)\ r_0^2\ \frac{1}{r}\ \frac{df}{dr}\\
f(r) &= \left(1 + \exp\{\frac{r-R}{a}\}\right)^{-1}
\end{aligned}$$

Here $R = r_0 A^{1/3}$, $r_0 = 1.27$ fm, $a = 0.67\,\mathrm{fm}$, $V_0 = (-51 \pm 33\frac{N-Z}{A})$ MeV (upper sign for neutrons, lower for protons), and $V_{ls} = -0.44V_0$

For protons add Coulomb potential (uniformly charged ball)

$$V_{\mathrm{C}}(r) = \begin{cases} 3/2(Z-1)\frac{e^2}{R}(1 - \frac{r^2}{3R^2}), & r \le R \\ (Z-1)\frac{e^2}{R} & r > R \end{cases}, \tag{24}$$

20.4 Fundamental symmetries

- Parity transformation: (After [Hol95])

$$\mathbf{r} \to -\mathbf{r} \tag{25}$$
$$\sigma \to \sigma \tag{26}$$
$$\mathbf{l} \to \mathbf{l} \tag{27}$$

- Time reversal:

$$t \to -t \tag{28}$$
$$\mathbf{r} \to r \tag{29}$$
$$\mathbf{p} \to -\mathbf{p} \tag{30}$$
$$L \to -L, \tag{31}$$
$$\sigma \to -\sigma \tag{32}$$

  Also in the scattering processes the initial and final states are swapped [Hol95], p. 90. T-revesrsal for molecules: "in the abscense of the external B-field the Hamiltonian would contain only even combinations of the angular momentum operators, e.g. $F_\alpha F_\beta$, $F_\alpha L_\beta$, $F_\alpha S_\beta$. Thus changing the signs of all the angular momentua should result in the same wave function." (Wigner group theory + p.396 of Drake)

- Charge conjugation:

  There is a nice table (Table 6.1) in the Jackson (Jac99) IIIrd edition with the transformation properties of various E&M-related quantities.

20.5 Parity violation in atoms (PNC/APV)

Leading effect are neutral current interactions.
Fermi constant $G_F = 2.22 \times 10^{-14}$ a.u.
Notations

$$\gamma^0 = \beta, \gamma^i = \alpha_i, \gamma_5 = i\gamma^0\gamma^1\gamma^2\gamma^3, \bar{\phi} = (\phi)^+\gamma_4$$

Weak charge

$$Q_W = Z(1 - 4\sin^2\theta_W) - N,$$

where Z is the number of protons, N number of protons, and θ_W is Weinberg angle, $\sin^2\theta_W \approx 1/4$, so that $Q_W \approx -N$.
Interactions :
The dominant effect is the **exchange of virtual Z^0 boson** b/w quark in the nucleus and atomic electron. Time-like part dominates

$$h_W = \frac{G_F}{2\sqrt{2}} Q_W \rho_{\text{nuc}}(\mathbf{r})\gamma_5$$

Angular reduction

$$\langle m|h_W|n\rangle = -i\frac{G_F}{2\sqrt{2}} Q_W \delta_{\kappa_m,-\kappa_n}\delta_{m_m,m_n}\int_0^\infty \rho_{\text{nuc}}(r)\left\{-G_m(r)F_n(r) + G_n(r)F_m(r)\right\}dr$$

20.6 Nuclear spin-dependent effects

1. Interaction b/w the nuclear axial-vector current and the electron vector-current from Z^0 exchange :

$$h_W^{(2)} = -\frac{G}{\sqrt{2}} K_2 \frac{\kappa - 1/2}{I(I+1)} \alpha \cdot \mathbf{I}\, \rho(r)$$

2. Anapole-electron interaction :

$$h_W^{a} = \frac{G}{\sqrt{2}} K_a \frac{\kappa}{I(I+1)} \alpha \cdot \mathbf{I}\, \rho(r)$$

Electron-electron weak interaction : $Z^{(0)}$ exchange b/w e. Contact interaction.

$$C_{1e} \approx -\frac{1}{2}(1 - 4\sin^2\theta_W), \tag{33}$$

$$C_{2e} \approx \frac{1}{2}. \tag{34}$$

Only cross term $C_{1e}C_{2e}$ contributes to PNC.

$$g^w_{ijkl} = \sqrt{2}G \int \bar{\phi}_i(\gamma_\mu C_{1e} + \gamma_\mu\gamma_5 C_{2e})\phi_k \bar{\phi}_j(\gamma^\mu C_{1e} + \gamma^\mu\gamma_5 C_{2e})\phi_l d^3x$$

20.7 Permanent electric-dipole moments

Permanent electric-dipole moments (EDM) may arise due to

1. nuclear Schiff moment,
2. intrinsic dipole moment of electron,
3. P,T-odd electron-nucleon interactions.P,T-odd semileptonic interactions

20.7.1 Schiff moment

Schiff moment $\mathbf{S}$ is aligned along the nuclear spin, $\mathbf{S} = S\frac{\mathbf{I}}{I}$. The corresponding Hamiltonian of interaction of atomic electron with the nuclear Schiff moment is

$$H_{SM} = 4\pi \mathbf{S} \cdot \nabla\rho\,(r) = \sum_\mu (-1)^\mu\, S_{-\mu}\ \left(H^e_{SM}\right)_\mu,$$

$$H^e_{SM} = 4\pi \nabla\rho\,(r)$$

where $\rho\,(r)$ is the nuclear density. An alternative expression, more suitable for relativistic calculations has been introduced in [FG02]

$$H^{e\prime}_{SM} = 3\frac{1}{B_4}\rho\,(r)\ \mathbf{r},$$

where $B_4 = \int_0^\infty r^4 \rho\,(r)\,dr$ is the fourth-order moment of the nuclear distribution.

For a closed-shell atom, at the HF level the induced dipole moment is

$$\mu = -\mathbf{S}\,\frac{2}{3}\sum_{am}(-1)^{j_a-j_m}\,\frac{\langle a||\mathbf{r}||m\rangle\langle m||H^e_{SM}||a\rangle}{\varepsilon_a-\varepsilon_m}$$

Taking into account that

$$\nabla\rho\,(r) = \frac{d\rho}{dr}\hat{r},$$
$$\hat{r}_\mu = C_{1\mu}\,(\hat{r})\,,$$

the relevant reduced matrix element is given by

$$\langle n_a\kappa_a||H^e_{SM}||n_b\kappa_b\rangle = 4\pi\langle\kappa_a||C_1||\kappa_b\rangle\int_0^\infty\left(G_a\,(r)\,G_b\,(r)+F_a\,(r)\,F_b\,(r)\right)\frac{d\rho}{dr}dr.$$

The nuclear density is parametererized as the Fermi distribution

$$\rho(r) = \frac{\rho_0}{1+e^{((r-c)/a)}}$$

Numerically the integration will be unstable, because the derivative of $\rho(r)$ will behave like a δ-function centered about cutoff radius c. More stable is the reduced matrix element of the finite nucleus SM

$$\langle n_a\kappa_a||H^{e'}_{SM}||n_b\kappa_b\rangle = 3\langle\kappa_a||C_1||\kappa_b\rangle\frac{1}{B_4}\int_0^\infty r\,\rho\,(r)\left(G_a\,(r)\,G_b\,(r)+F_a\,(r)\,F_b\,(r)\right)dr$$

20.7.2 P,T-odd electron-nucleon tensor interaction

Parametrization [MP85]

$$h^T = \sqrt{2}G_F\,C_{TN}\;\sigma_N\cdot\left(i\gamma_0\gamma_5\,\sigma\right)_e\rho_N\,(\mathbf{r}_e)\;. \tag{35}$$

Here $G_F \approx 2.22254\times10^{-14}$ a.u. is the Fermi constant and C_{TN} is the coupling constant of interest. The induced atomic EDM is

$$\mu = \sum_i\frac{\langle\Psi_0|\mathbf{D}|\Psi_i\rangle\langle\Psi_i|h_T|\Psi_0\rangle}{E_0-E_i}+\sum_i\frac{\langle\Psi_0|h_T|\Psi_i\rangle\langle\Psi_i|\mathbf{D}|\Psi_0\rangle}{E_0-E_i} \tag{36}$$

At the Hartree-Fock level

$$\mu = \sum_{am}\frac{\langle a|\mathbf{D}|m\rangle\langle m|h_T|a\rangle}{\varepsilon_a-\varepsilon_m}+c.c. \tag{37}$$

where a runs over occupied and m over excited single-particle orbitals and $c.c.$ term is obtained by swapping D and h^T.

The result of angular reduction for closed-shell atom

$$\mu_\lambda = (\sigma_N)_\lambda \sqrt{2} G_F C_{TN} \frac{1}{3} \sum_{am} (-1)^{j_a - j_m} \frac{\langle a||\mathbf{D}||m\rangle \langle m||\left(i\gamma_0\gamma_5 \sigma_e\right) \rho_N\left(\mathbf{r}_e\right)||a\rangle}{\varepsilon_a - \varepsilon_m} + c.c. = \tag{38}$$

$$- (\sigma_N)_\lambda \sqrt{2} G_F C_{TN} \frac{2}{3} \sum_{am} (-1)^{j_a - j_m} \frac{\langle a||\mathbf{r}||m\rangle \langle m||\left(i\gamma_0\gamma_5 \sigma_e\right) \rho_N\left(\mathbf{r}_e\right)||a\rangle}{\varepsilon_a - \varepsilon_m} \tag{39}$$

where we took into account that $\mathbf{D} = -|e|\mathbf{r}$. Reduced matrix element of a combination $\left(i\gamma_0\gamma_5 \sigma\right) \rho_N\left(\mathbf{r}_e\right)$ is given as

$$\langle n_a \kappa_a||\left(i\gamma_0\gamma_5 \sigma\right) \rho_N\left(\mathbf{r}_e\right)||n_b \kappa_b\rangle =$$
$$- \int_0^\infty \rho_N(r)\, dr \left\{\langle \kappa_a||\sigma||-\kappa_b\rangle G_a(r) F_b(r) + \langle -\kappa_a||\sigma||\kappa_b\rangle F_a(r) G_b(r)\right\} \tag{40}$$

Here $G(r)$ and $F(r)$ are the large and small components of the radial wavefunctions. Since $\langle \kappa_m||\sigma||\kappa_n\rangle \propto \delta_{l_m l_n}$ and $l_{-\kappa} = 2j - l_\kappa$, the selection rule for the first term is $l_a + l_b = 2j_b$ and for the second term $l_a + l_b = 2j_a$. Apparently, the states a and b must have opposite parities. Another selection rule is $\Delta(j_a, 1, j_b)$. Also

$$\langle \kappa_a||\sigma||\kappa_b\rangle = \delta_{l_a l_b} (-1)^{l_a + j_a - 1/2} \sqrt{[j_a, j_b]} \sqrt{6} \left\{ \begin{array}{ccc} 1 & j_a & j_b \\ l_a & 1/2 & 1/2 \end{array} \right\} \tag{41}$$

20.8 Intrinsic dipole moment of the electron

The SM limit

$$d_{\mathrm{SM}}\left(e^-\right) = 10^{-38} \text{e cm}$$

Best present (2004) limit

$$d\left(Tl, e^-\right) \sim 1.6 \times 10^{-27} \text{e cm}$$

Matrix elements for the electron EDM operator.

The coupling of the electron EDM d_e with the E-field is

$$H_d = 2 d_e \left(\begin{array}{cc} 0 & 0 \\ 0 & (\sigma \cdot \mathbf{E}) \end{array} \right)$$

We assume that the field is produced by the spherically-symmetric charge distribution inside the atom. Then

$$\mathbf{E} = - \left(\frac{d}{dr} V\right) \hat{\mathbf{r}}$$

Using

$$(\sigma \cdot \hat{\mathbf{r}})\, \Omega_{\kappa m}(\hat{r}) = -\Omega_{-\kappa m}(\hat{r}),$$

and the orthogonality of the spherical spinors, we arrive at

$$\langle a|H_d|b\rangle = \left\{2d_e \int_0^\infty dr\ Q_a(r)\left(\frac{dV}{dr}\right)Q_b(r)\right\}\delta_{\kappa_a,-\kappa_b}\delta_{m_a,m_b}.$$

The angular selection rules in this integral are simply due to the fact that H_d is a pseudoscalar.

21 Scattering theory

21.1 Asymptotic expansion

$$\Psi_k^{(+)} \cong N\left(e^{i\mathbf{k}\cdot\mathbf{r}} + f_k(\hat{r})\frac{e^{ikr}}{r}\right)$$

$f_k(\hat{r})$ is the scattering amplitude. Differential scattering cross-section

$$\frac{\#\text{ of scattered particles into } 2\pi r^2 d\Omega}{\text{total }\#\text{ of incident particles}} = \frac{d\sigma}{d\Omega} = |f_k(\hat{r})|^2$$

Total scattering cross-section

$$\sigma = \int |f_k(\hat{r})|^2 d\Omega$$

The # of particles per unit time per unit area is found using current-density formula

$$j = \frac{\hbar}{2\mu}\frac{1}{i}\left(\psi^*\nabla\psi - \psi\nabla\psi^*\right).$$

Optical theorem: the scattering amplitude in the forward direction and the total x-section are related as

$$\sigma = \frac{4\pi}{k}\,\mathrm{Im}\ \ f_k(0)\ .$$

21.2 Lippman-Schwinger integral equation and Green's functions

$$\begin{aligned}
\left(\nabla^2 + k^2\right)\Psi(\mathbf{r}) &= U(\mathbf{r})\,\Psi(\mathbf{r}) \\
U(\mathbf{r}) &= \frac{2m}{\hbar^2}V(\mathbf{r}) \\
\Psi &= Ne^{i\mathbf{k}\cdot\mathbf{r}} - \frac{1}{4\pi}\int G(\mathbf{r},\mathbf{r}')\,U(\mathbf{r}')\,\Psi(\mathbf{r}')\,d\mathbf{r}' \\
\left(\nabla^2 + k^2\right)G(\mathbf{r},\mathbf{r}') &= -4\pi\delta(\mathbf{r}-\mathbf{r}') \\
G^{(\pm)}(\mathbf{r},\mathbf{r}') &= \frac{\exp(\pm ik|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}
\end{aligned}$$

21.3 Born approximation

$$f_{\mathbf{k}}\left(\hat{\mathbf{k}}'\right) \approx -\frac{m}{2\pi\hbar^2}\int e^{-i\mathbf{k}'\cdot\mathbf{r}}V\left(\mathbf{r}'\right)e^{i\mathbf{k}\cdot\mathbf{r}'}d\mathbf{r}'$$

For spherically symmetric potentials $V\left(\mathbf{r}\right) \equiv V\left(|\mathbf{r}|\right)$ this expression simplifies to

$$f\left(\theta\right) = -\frac{2m}{\hbar^2}\int_0^\infty V\left(r'\right)\frac{\sin qr}{qr'}\left(r'\right)^2 dr',$$

where θ is the angle between $\mathbf{k}$ and $\mathbf{k}'$, $\mathbf{q} = \mathbf{k}' - \mathbf{k}$

$$q = 2k\ \sin\frac{\theta}{2}$$

21.4 Partial wave expansion

21.4.1 Spherical waves

Free particles (relativistic expansion):

$$\Psi_{pjl}\left(\mathbf{r}\right) = \frac{1}{\sqrt{2\varepsilon}}\begin{pmatrix} \sqrt{\varepsilon+m}\,R_{pl}\left(r\right)\,\Omega_{jlm}\left(\hat{r}\right) \\ -\sqrt{\varepsilon-m}\,R_{pl'}\,\left(r\right)\Omega_{jl'm}\left(\hat{r}\right) \end{pmatrix},\ l' = 2j - l$$

$$\varepsilon = +\sqrt{p^2+m^2}$$

$$R_{pl}\left(r\right) = \sqrt{\frac{2\pi p}{r}}J_{l+1/2}(pr)$$

Plane wave

$$e^{i\mathbf{k}\cdot\mathbf{r}} = \sum_{l=0}^{\infty}\left(2l+1\right)i^l j_l\left(kr\right)P_l\left(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}\right)$$

$$\exp\left[i\mathbf{k}\cdot\mathbf{r}\right] = 4\pi\sum_{lm} i^l j_l\left(kr\right)Y_{lm}^*\left(\hat{k}\right)Y_{lm}\left(\hat{r}\right)$$

$$\exp\left[-i\mathbf{k}\cdot\mathbf{r}\right] = 4\pi\sum_{lm} i^{-l} j_l\left(kr\right)Y_{lm}\left(\hat{k}\right)Y_{lm}^*\left(\hat{r}\right)$$

$$Y_{l0}\left(\theta,\phi\right) = \sqrt{\frac{2l+1}{4\pi}}P_l\left(\cos\theta\right)$$

We have to solve

$$H\Psi^{(+)} = 2\mu k^2\Psi^{(+)}$$

$\Psi^{(+)}$ is expanded into a complete set of sperical harmonics and radial wavefunctions $R_{kl} = \frac{u_{kl}}{r}$

$$\Psi^{(+)} = \sum c_{lm}R_{kl}\left(r\right)Y_{l0}\left(\theta\right) \tag{42}$$

u_{kl} are solutions of radial S.E. *regular* at the origin ($u_{kl}(0) \to 0$)

$$\left(-\frac{1}{2\mu}\frac{d^2}{dr^2} + U(r)\right) u_{kl} = 2\mu k^2 u_{kl}$$

At large r

$$u_{kl} \sim \sin\left(kr - l\frac{\pi}{2} + \delta_l\right)$$

δ_l are the phase shifs due to (short-range) potential U, and $-l\frac{\pi}{2}$ is a free-particle phase-shift. By matching partial-wave expansion of Eq.**??** with Eq. 42 at large r, one obtains

$$f(\theta) = \sum [l] \quad f_l P_l(\cos\theta)$$

with

$$f_l = \frac{1}{2ik}\left(e^{2i\delta_l} - 1\right) = \frac{1}{k}(2l+1)\, e^{i\delta_l} \sin\ \delta_l$$

Total cross section

$$\sigma = \frac{4\pi}{k^2}\sum_{l=0}^{\infty} [l] \sin^2 \delta_l(k)$$

The stationary scattering wavefunction is represented as (plane wave + outgoing spherical wave)

$$\Psi^{(+)} = N \sum [l] \frac{u_{kl}(r)}{kr} \exp\left[i\left(\frac{\pi}{2}l + \delta_{lk}\right)\right] P_l(\cos\theta)$$

As a check if the potential is absent $\delta_{lk} = 0$, $\frac{u_{kl}(r)}{kr} = j_l(kr)$, and we obtain $f_l = 0$, $\sigma = 0$, and

$$\Psi^{(+)}_{\text{free particle}} = N \sum [l]\, j_l(kr) \exp\left[i\left(\frac{\pi}{2}l\right)\right] P_l(\cos\theta)$$

i.e. the partial-wave expansion of the plane wave $N\, e^{ikz}$.

22 Electrostatics

Uniform magnetic field (Both MKSA and Gaussian units)

$$\mathbf{A} = \frac{1}{2}\mathbf{B} \times \mathbf{r}$$

23 Electrodynamics & lasers

Maxwell's equations (Gaussian units. See Section 3.2 for other system-of-units)

$$\begin{aligned} \nabla \cdot \mathbf{E} &= 4\pi\rho \\ \nabla \times \mathbf{H} &= \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t} + \frac{4\pi}{c}\mathbf{j} \\ \nabla \cdot \mathbf{H} &= 0 \\ \nabla \times \mathbf{E} &= -\frac{1}{c}\frac{\partial \mathbf{H}}{\partial t} \end{aligned}$$

Energy density W and energy flux (Poynting vector) $\mathbf{S}$

$$\begin{aligned} \frac{\partial W}{\partial t} + \nabla \cdot \mathbf{S} &= 0 \\ W &= \frac{1}{8\pi}\left(\mathbf{E}^2 + \mathbf{H}^2\right) \\ \mathbf{S} &= \frac{c}{4\pi}\mathbf{E} \times \mathbf{H} \end{aligned}$$

Vector $\mathbf{A}$ and scalar φ potentials

$$\begin{aligned} \mathbf{H} &= \nabla \times \mathbf{A} \\ \mathbf{E} &= -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} - \nabla\varphi \end{aligned}$$

Electromagnetic wave

$$\begin{aligned} \mathbf{A} &= A_0\hat{\varepsilon}\cos\left(\omega t - kr\right) \\ k &= \omega/c \\ |\mathcal{E}_0| &= |\mathcal{H}_0| = kA_0 \\ I &= \langle S \rangle = \frac{c}{8\pi}k^2A_0^2 = \frac{c}{8\pi}\mathcal{E}_0^2 \end{aligned}$$

Here I is the laser intensity (notice averaging of the flux over time). Atomic units of electric field and intensity

$$\begin{aligned} \mathcal{E}_0 &= m^2e^5/\hbar^4 = 5.14220826 \times 10^{11}\ V/m \\ I_0 &= c\mathcal{E}_0^2 = \ ???\ W/cm^2 \end{aligned}$$

Relation b/w intensity and the field strength of the laser

$$I_0 \left[\frac{\mathrm{mW}}{\mathrm{cm}^2}\right] = 1.33 \left(\mathcal{E}\,[\mathrm{V/cm}]\right)^2$$

Relation b/w CGSE and SI units of electric field

$$1\mathrm{esu}\ (E) \approx 300\ \mathrm{V/cm}$$

Polarization vector:

$$\hat{\varepsilon} = e_x \cos\theta + i e_y \sin\theta = -\frac{1}{\sqrt{2}}\left(\cos\theta + \sin\theta\right) e_{+1} + \frac{1}{\sqrt{2}}\left(\cos\theta - \sin\theta\right) e_{-1}$$
$$\hat{\varepsilon}^* = e_x \cos\theta - i e_y \sin\theta = -\frac{1}{\sqrt{2}}\left(\cos\theta - \sin\theta\right) e_{+1} + \frac{1}{\sqrt{2}}\left(\cos\theta + \sin\theta\right) e_{-1}$$

The parametric angle θ may be related to ellipticity parameter ζ, employed in Ref.[MOR86] as

$$\cos\theta = \frac{1}{\sqrt{1+\zeta^2}}$$
$$\sin\theta = \frac{\zeta}{\sqrt{1+\zeta^2}}$$

These authors also introduced degree of linear

$$l = \frac{1-\zeta^2}{1+\zeta^2} = \cos 2\theta$$

and circular

$$A = \frac{2\zeta}{1+\zeta^2} = \sin 2\theta$$

polarization. Notice (Scalar product is without complex conjugation!)

$$\begin{aligned} \left(\hat{\varepsilon}^* \cdot\ \hat{\varepsilon}\right) &= 1 \\ \left[\hat{\varepsilon}^* \times\ \hat{\varepsilon}\right]_\mu &= \delta_{\mu,0} \sin 2\theta \\ \left\{\hat{\varepsilon}^* \otimes\ \hat{\varepsilon}\right\}_{2\mu} &= -\frac{1}{\sqrt{6}}\delta_{\mu,0} + \frac{1}{2}\cos 2\theta\ \delta_{\mu,\pm 2} \end{aligned} \tag{43}$$

24 Laser-atom interaction

Two-level system.

Level 0 lives forever and k has radiative lifetime of τ_k due to radiative decay to level 0. The x-section of absorption of the photon is given by

$$\sigma_a = 2\pi \frac{c^2}{\omega^2} \frac{g_k}{g_0} \frac{\Gamma^2}{\Delta^2 + \Gamma^2\left(1+\chi\right)}$$

where

$$\Delta = \omega - \omega_{k0}$$
$$\Gamma = \frac{1}{2}\frac{1}{\tau_k}$$
$$\chi = 2\left(\frac{\tau_k}{\hbar}\right)^2 |\mathbf{D}_{k0}\cdot\mathbf{E}|^2$$

Steady-state population of the excited state

$$\rho_{kk} = \frac{\chi}{2}\frac{\Gamma^2}{\Delta^2 + \Gamma^2(1+\chi)}$$

Level 0 and k have lifetimes τ_0 and τ_k. τ_{k0} is the lifetime of k due to decay to 0. The x-section of absorption of the photon is given by

$$\sigma_a = \pi\frac{c^2}{\omega^2}\frac{g_k}{g_0}\frac{\tau_k}{\tau_{k0}}\frac{\Gamma^2}{\Delta^2 + \Gamma^2(1+\chi)}$$

where detunnig from the resonance

$$\Delta = \omega - \omega_{k0}$$
$$\Gamma = \frac{1}{2}\left(\frac{1}{\tau_0} + \frac{1}{\tau_k}\right)$$
$$\chi = \frac{\tau_0\tau_k}{\hbar^2}|\mathbf{D}_{k0}\cdot\mathbf{E}|^2$$

χ is called saturation parameter and D is the E1-mel, E is the laser field strength. Degeneracies $g_l = 2J_l + 1$.

24.1 Stark effect in the laser field

Following Ref.[MOR86]. For a linearly polarized laser, the level shift is

$$\Delta E_{nJM} = -\frac{\mathcal{E}^2}{4}\left(\alpha^S_{nJ}(\omega) + \alpha^T_{nJ}(\omega)\frac{3M^2 - J(J+1)}{2J(2J-1)}\right)$$

where scalar and tensor dynamic polarizabilities

$$\alpha^S_{nJ}(\omega) = \frac{1}{3[J]}\sum_{J'} S^{J'}_{nJ}(\omega)$$

$$\alpha^T_{nJ}(\omega) = \frac{1}{3\sqrt{[J]}}\sqrt{\frac{2J(2J-1)}{(J+1)(2J+3)}}\sum_{J'}(-1)^{J+J'}\left\{\begin{array}{ccc} 1 & 1 & 2 \\ J & J & J' \end{array}\right\} S^{J'}_{nJ}(\omega)$$

Here the reduced sums are defined as

$$S^{J'}_{nJ}(\omega) = 2\sum_{n'}|\langle nJ||D||n'J'\rangle|^2\left\{\frac{E_{n'} - E_n}{(E_{n'} - E_n)^2 - \omega^2}\right\}.$$

Notice that depending on the detuning of the laser from the position of the atomic resonance, the reduced sums may accept both negative and positive values.

25 Hyperfine interaction

The coupling with the nuclear fields

$$H_{\text{hfs}} = \sum_k \left(\mathcal{N}^{(k)} \cdot \mathcal{T}^{(k)} \right)$$

Here ITOs $\mathcal{N}^{(k)}$ and $\mathcal{T}^{(k)}$ act in the space of nuclear and electronic coordinates respectively, k being their ranks. The nuclear magnetic moment is conventionally defined as

$$\mu = \langle I, M_I = I | \mathcal{N}_0^{(1)} | I, M_I = I \rangle = \begin{pmatrix} I & 1 & I \\ -I & 0 & I \end{pmatrix} \langle I || \mathcal{N}^{(1)} || I \rangle = \sqrt{\frac{2I}{(2I+1)(2I+2)}} \langle I || \mathcal{N}^{(1)} || I \rangle,$$

and the nuclear electric quadrupole moment as (notice the factor of 2)

$$Q = 2\langle I, M_I = I | \mathcal{N}_0^{(2)} | I, M_I = I \rangle = 2 \frac{(2I)!}{\sqrt{(2I-2)!\,(2I+3)!}} \langle I || \mathcal{N}^{(2)} || I \rangle$$

The (one-particle) electronic tensors are

$$\mathcal{T}_\lambda^{(1)} = -\frac{|e|}{4\pi\varepsilon_0} \frac{i\sqrt{2} \left(\alpha \cdot \mathbf{C}_{1\lambda}^{(0)} (\hat{\mathbf{r}}) \right)}{cr^2}$$
$$\mathcal{T}_\lambda^{(2)} = -\frac{|e|}{4\pi\varepsilon_0} \frac{C_\lambda^2 (\hat{\mathbf{r}})}{r^3}$$

25.1 Interaction with the static electric field

A typical strength of laboratory E-field

$$\mathcal{E}_{\text{lab}} = 1 \text{ kV/cm} = 10^5 V/m = 10^5 / \left(0.51422082 \times 10^{12} \right) a.u. = 2 \times 10^{-7} a.u.$$

26 Commutator identities

Uncertainty relation. For two Hermitian operators with non-vanishing commutator $[A, B] = iC$

$$\Delta A \Delta B \geq \frac{1}{2} \left| \langle C \rangle \right|,$$

where $\Delta A = \sqrt{\langle (A - \langle A \rangle)^2 \rangle}$.

A and B are operators, λ is a c-number.

$$[A, B^n] = nB^{n-1} [A, B]$$
$$[A^n, B] = nA^{n-1} [A, B]$$
$$[AB, C] = A [B, C] + [A, C] B$$
$$[A, BC] = [A, B] C + B [A, C]$$

$$[\sum_i A_i, \sum_k B_k] = \sum_{ik} [A_i, B_k]$$

$$(A - \lambda B)^{-1} = A^{-1} + \lambda A^{-1} B A^{-1} + \lambda^2 A^{-1} B A^{-1} B A^{-1} + \cdots$$

$$\exp(A) B \exp(-A) = B + [AB] + \frac{1}{2!}[A[AB]] + \frac{1}{3!}[A[A[AB]]] + \cdots$$

The identity below holds only if $[A,[C,A]] = [A,[C,B]] = [B,[C,B]] = 0$, with $C \equiv [A,B]$ (Ref. [Hol95]).

$$\exp(A+B) = \exp(A)\exp(B)\exp(-\frac{[A,B]}{2})\exp(\frac{[A,[A,B]]}{6})$$

27 Abbreviations

CC - Coupled Cluster

MCHF - Multi-Configurational Hartree-Fock

MCSCF - Multi-Configurational Self-Consistent Field

CI - Configuration - Interaction

28 Mathematics

28.1 Dirac δ function and friends

$$\int_0^\infty e^{i\alpha\xi} d\xi = 2\pi\delta(\alpha)$$

$$\int \frac{f(x)dx}{x - a - i0} = \mathfrak{P} \int \frac{f(x)dx}{x-a} + i\pi f(a)$$

$$\delta[\phi(x)] = \sum_i \frac{1}{|\phi'(x_i)|} \delta(x - x_i)$$

$$\delta[a\ x] = \frac{1}{|a|}\delta(x) \quad , \ \delta(-x) = \delta(x)$$

$$\int d^3k\ \exp[i\mathbf{k}\cdot\mathbf{r}] = (2\pi)^3 \delta(\mathbf{r})$$

$$\frac{1}{(\varepsilon - E)^n} = \frac{1}{2}\left(\frac{1}{(\varepsilon - E + i0)^n} + \frac{1}{(\varepsilon - E - i0)^n}\right)$$

$$= \frac{1}{(n-1)!}\frac{d^{n-1}}{dE^{n-1}} P \frac{1}{\varepsilon - E}$$

$$\delta(\mathbf{r}) = ...r^2 \delta(r)$$

Derivatives of the δ function

$$\frac{\delta(x)}{x^n} = (-1)^n \delta^{(n)}(x)$$
$$\int_{-\infty}^{+\infty} f(x)\,\delta^{(n)}(x) = (-1)^n f^{(n)}(0)$$

28.2 Legendre polynomials

Any function of the angle may be expanded in terms of the Legendre polynomials $P_l(\cos\theta)$

$$f(\theta) = \sum_{l=0} b_l P_l(\cos\theta)$$
$$b_l = \frac{2l+1}{2}\int_0^{\pi} f(\theta)\,P_l(\cos\theta)\sin\theta\,d\theta$$

Notice the additional factor in front of the integral; it arises because the P_l are not normalized.

$$P_l(\cos\theta) = C_{l0}(\theta,\phi) = \sqrt{\frac{4\pi}{2l+1}}Y_{l0}(\theta,\phi)$$

Spherical Bessel j_l, Neumann n_l, and Hankel h_l functions

$$j_l(z) \equiv \sqrt{\frac{\pi}{2z}}J_{l+1/2}(z)$$

Asymptotic formulae

$$j_l(z) \simeq \begin{cases} \frac{2^l\ l!}{(2l+1)!}z^l + O\left(z^{l+2}\right), & z \ll 1 \\ \frac{1}{z}\cos\left(z-(l+1)\frac{\pi}{2}\right) & z \gg l \end{cases}$$
$$n_l(z) \simeq \begin{cases} -\frac{(2l-1)!!}{z^{l+1}}, & z \ll 1 \\ \frac{1}{z}\sin\left(z-(l+1)\frac{\pi}{2}\right) & z \gg l \end{cases}$$

$$h_l^{(1,2)}(z) = h_l^{\pm}(z) = j_l(z) \pm i\,n_l(z) \simeq \begin{cases} & z \ll 1 \\ \mp\frac{1}{z}\exp\left[\pm i\left(z-(l+1)\,\pi/2\right)\right] & z \gg 1 \end{cases}$$

Useful identity $(2l-1)!! = (2l)!/(2^l l!)$.

28.3 Vector analysis

The following identities are useful for an arbitrary regular function of $r = |\mathbf{r}|$. (see, e.g., Jackson)

$$\nabla f(r) = \frac{\partial f(r)}{\partial r}\frac{\mathbf{r}}{r}$$
$$\nabla\cdot\left[\frac{\mathbf{r}}{r}f(r)\right] = \frac{2}{r}f(r) + \frac{\partial f(r)}{\partial r}$$

In particular

$$\nabla \frac{1}{r} = -\frac{\mathbf{r}}{r^3}$$
$$\nabla r = \frac{\mathbf{r}}{r}$$

Also from the Gauss' law

$$\nabla^2 \frac{1}{r} = -4\pi\delta(\mathbf{r})$$

Taylor series

$$\mathbf{A}(\mathbf{r}+\mathbf{a}) = e^{(\mathbf{a}\cdot\nabla)}\ \mathbf{A}(\mathbf{r})$$

Divergence theorem

$$\int_V \nabla\cdot\mathbf{j}\ dV = \oint_S \mathbf{j}\cdot\mathbf{dS}$$

Green's first identity

$$\int_V \left(\phi\nabla^2\psi + \nabla\phi\cdot\nabla\psi\right)\ dV = \oint_S \phi\frac{\partial\psi}{\partial n}dS,$$

where $\frac{\partial\psi}{\partial n}$ is the normal derivative (directed outwards from inside the volume V).

Green's second identity (Green's theorem)

$$\int_V \left(\phi\nabla^2\psi - \psi\nabla^2\phi\right)\ dV = \oint_S \left(\phi\frac{\partial\psi}{\partial n} - \psi\frac{\partial\phi}{\partial n}\right)dS.$$

28.4 Vector identities

$$\mathbf{A}\ \times\ (\mathbf{B}\ \times\ \mathbf{C}) = \mathbf{B}(\mathbf{A}\cdot\ \mathbf{C}) -\ \mathbf{C}(\mathbf{A}\cdot\ \mathbf{B})$$

28.5 Cauchi's residue theorem

If $f(z)$ is analytical function, except for a finite number of singularities a_1, a_2, $...a_n$ inside a region bounded by a curve C, then

$$\oint_{\circlearrowleft C} f(z)\,dz = 2\pi i\sum_k \operatorname{Res} f(z)$$

For a function

$$f(z) = \frac{c_{-m}}{(z-a)^m} + \cdots\frac{c_{-1}}{(z-a)} + \sum_{k=0}^{\infty} c_k (z-a)^k$$

the residue is the coefficient c_{-1}. It may be computed as

$$c_{-1} = \frac{1}{(m-1)!}\lim_{z\to a}\frac{d^{m-1}}{dz^{m-1}}\left((z-a)^m f(z)\right)$$

28.6 Groups (following Edmonds[Edm85])

Designations for common continious groups

1. $GL(n)$ all linear transformations in n-dimensional space (complex $n \times n$ matrixes a);
2. $U(n)$ all unitary transformations, a are unitary matrixes;
3. $SU(n)$ special unitary group, det $a = +1$;
4. $O(n)$ orthogonal group: real matrices a (rotations and reflections, det $a = \pm 1$);
5. $SO(n)$ real unitary matrices a, det $a = +1$

Representation of degree n of a group G: to every element a is assigned $n \times n$ matrix $T(a)$ so that

$$T(a) \cdot T(b) = T(ab)$$

Equivalent representation is obtained via linear transformation S, then the group element a may be represented by $S^{-1} \cdot T(a) \cdot S$

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