

PHYSICS OF ATOMS AND MOLECULES

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Atoms and Electromagnetic Interaction

$\mathbf{A}(\mathbf{r}, t)$ is the vector potential, then in free space the fields are:

$$\mathbf{E}(\mathbf{r}, t) = -\frac{\partial}{\partial t} \mathbf{A}(\mathbf{r}, t), \quad \mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t)$$

We use the Coulomb gauge, $\nabla \cdot \mathbf{A} = 0$. From Maxwell:

$$\nabla^2 \mathbf{A} - \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} = 0 \rightarrow \mathbf{A} = A_0(\omega) \hat{\mathbf{e}} \cos(\mathbf{k} \cdot \mathbf{r} - \omega t + \delta_\omega)$$

With $\hat{\mathbf{e}} \cdot \mathbf{k} = 0$ in the Coulomb gauge and generally $\omega = |\mathbf{k}|c$.

The derived electromagnetic fields:

$$\mathbf{E}(\mathbf{r}, t) = -\omega A_0(\omega) \hat{\mathbf{e}} \sin(\mathbf{k} \cdot \mathbf{r} - \omega t + \delta_\omega)$$

$$\mathbf{B}(\mathbf{r}, t) = -A_0(\omega) (\hat{\mathbf{k}} \times \hat{\mathbf{e}}) \sin(\mathbf{k} \cdot \mathbf{r} - \omega t + \delta_\omega)$$

The time averaged energy density of this wave is given by:

$$\rho(\omega) = \frac{1}{2} \left[\epsilon_0 \langle |\mathbf{E}|^2 \rangle + \frac{1}{\mu_0} \langle |\mathbf{B}|^2 \rangle \right] = \frac{\epsilon_0 \omega^2 A_0^2(\omega)}{2} = \hbar \omega \frac{N(\omega)}{V}$$

So $A_0(\omega) = \sqrt{\frac{2\hbar}{\epsilon_0 \omega} \frac{N(\omega)}{V}}$. The intensity is $I(\omega) = \rho(\omega)c$.

Atom Interaction:

$$\begin{aligned} \text{The Hamiltonian is: } H &= \frac{1}{2m} (-i\hbar \nabla + e\mathbf{A})^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \\ &= -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} - \frac{i\hbar e}{m} \mathbf{A} \cdot \nabla + \frac{e^2}{2m} \mathbf{A}^2 \end{aligned}$$

since in Coulomb gauge $[\nabla, \mathbf{A}] = 0$. We neglect the \mathbf{A}^2 term under the weak field approximation, so $H = H_0 + H'$ with H_0

the Hydrogenic Hamiltonian and $H' = -(i\hbar e/m) \mathbf{A} \cdot \nabla$

Writing a general solution as: $\Psi = \sum_k c_k(t) \psi_k(\mathbf{r}) e^{-iE_k t/\hbar}$

Where ψ_k are normalized Hydrogenic functions, this gives

$$\text{coupled equations: } \dot{c}_b(t) = \frac{1}{i\hbar} \sum_k H'_{bk} c_k(t) e^{i\omega_{bk} t}$$

With $H'_{bk} = \langle \psi_b | H'(t) | \psi_k \rangle$ and $\omega_{bk} = (E_b - E_k)/\hbar$.

If for $t \leq 0$ the atom is in a defined state ψ_a , $c_k(t \leq 0) = \delta_{ka}$

and then: $c_b^{(1)}(t) = \frac{1}{i\hbar} \int_0^t H'_{ba}(t') e^{i\omega_{ba} t'} dt'$

And inserting a general vector potential we find:

$$c_b^{(1)}(t) = \frac{-e}{m} \int_0^t d\omega A_0(\omega) \left[e^{i\omega t} \langle \psi_b | e^{i\mathbf{k}\cdot\mathbf{r}} \hat{\mathbf{e}} \cdot \nabla | \psi_a \rangle \int_0^t dt' e^{i(\omega_{ba}-\omega)t'} + e^{-i\omega t} \langle \psi_b | e^{-i\mathbf{k}\cdot\mathbf{r}} \hat{\mathbf{e}} \cdot \nabla | \psi_a \rangle \int_0^t dt' e^{i(\omega_{ba}+\omega)t'} \right]$$

The first integral: $\hbar\omega_{ba} = E_b - E_a = \hbar\omega$, i.e absorption.

The second integral: $\hbar\omega_{ba} = E_b - E_a = -\hbar\omega$, i.e emission.

Einstein Coefficients: ($E_a < E_b$, $g_{a,b}$ - degeneracy)

$$\dot{N}_{a \rightarrow b} = B_{a \rightarrow b} g_a N_a \rho(\omega_{ba}), \quad \rho(\omega) = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/kT} - 1}$$

$$\dot{N}_{b \rightarrow a} = A_{b \rightarrow a} g_b N_b + B_{b \rightarrow a} g_b N_b \rho(\omega_{ba}), \quad N_a / N_b = e^{\hbar\omega_{ba}/kT}$$

Transition Rates:

For incoherent radiation and long enough times one can obtain:

$$W_{ba}^\pm = \frac{d}{dt} |c_b^{(1)}(t)|^2 = \frac{4\pi^2}{m^2 c} \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{I(\omega_{ba})}{\omega_{ba}^2} |M_{ba}^\pm(\omega_{ba})|^2$$

Where $M_{ba}^\pm = \langle \psi_b | e^{\pm i\mathbf{k}\cdot\mathbf{r}} \hat{\mathbf{e}} \cdot \nabla | \psi_a \rangle$, (+) is for absorption and

(-) for stimulated emission, but $M_{ba}^+ = M_{ba}^{*-}$ so $W_{ba}^+ = W_{ba}^-$.

Transition Rates: (contd.)

Rate of absorption of energy is $\hbar\omega_{ba} W_{ba}^+$ so the cross section for

$$\text{absorption is: } \sigma_{ba} = \frac{\hbar\omega_{ba} W_{ba}^+}{I(\omega_{ba})} = \frac{4\pi^2 \hbar^2 \alpha}{m^2 \omega_{ba}} |M_{ba}^+(\omega_{ba})|^2$$

Rate of spontaneous emission is obtained by replacing $I(\omega_{ba})$

with $I(\omega) = \hbar\omega c [N(\omega) + 1]/V$ and setting $N(\omega) = 0$:

$$d\bar{W}_{ba} = \frac{4\pi^2}{m^2} \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{\hbar}{V \omega_{ba}} |M_{ba}(\omega_{ba})|^2 \frac{V}{(2\pi)^3} \frac{\omega_{ba}^2}{c^3} d\Omega$$

where $\rho(\omega) d\omega d\Omega = \frac{V}{(2\pi)^3} k^2 dk d\Omega = \frac{V}{(2\pi)^3} \frac{\omega^2}{c^3} d\omega d\Omega$ is the

photon density of states. Summing over the two possible polarization states and all directions of emissions we find:

$$\bar{W}_{ba} = \frac{\omega_{ba}}{2\pi m^2 c^3} \left(\frac{e^2}{4\pi\epsilon_0} \right) \int d\Omega \sum_{\lambda=1}^2 |M_{ba}^\lambda(\omega_{ba})|^2$$

The Dipole Approximation:

The atom is very small compared with the wavelength of light, so $\mathbf{k} \cdot \mathbf{r} \ll 1$ and $e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1$ so:

$$M_{ba}^\pm(\omega_{ba}) = \hat{\mathbf{e}} \cdot \langle \psi_b | \nabla | \psi_a \rangle = \hat{\mathbf{e}} \cdot \frac{im}{\hbar} \langle \psi_b | \mathbf{r} | \psi_a \rangle$$

$$= \hat{\mathbf{e}} \cdot \frac{im}{\hbar} \frac{1}{i\hbar} \langle \psi_b | \mathbf{r} H_0 - H_0 \mathbf{r} | \psi_a \rangle = -\frac{m\omega_{ba}}{\hbar} \hat{\mathbf{e}} \cdot \mathbf{r}_{ba}$$

Defining θ as the angle between $\hat{\mathbf{e}}$ and \mathbf{r}_{ba} , we find:

$$W_{ba}^\pm = \frac{4\pi^2}{\hbar^2 c} \left(\frac{e^2}{4\pi\epsilon_0} \right) I(\omega_{ba}) |\mathbf{r}_{ba}|^2 \cos^2 \theta$$

For unpolarized isotropic light replace $\cos^2 \theta$ by average: 1/3.

For spontaneous emission we have:

$$\bar{W}_{ba} = \frac{\omega_{ba}^3}{2\pi \hbar^2 c^3} \left(\frac{e^2}{4\pi\epsilon_0} \right) \int d\Omega \sum_{\lambda=1}^2 |\hat{\mathbf{e}}_\lambda \cdot \mathbf{r}_{ba}|^2 = \frac{4\omega_{ba}^3}{3\hbar^2 c^3} \left(\frac{e^2}{4\pi\epsilon_0} \right) |\mathbf{r}_{ba}|^2$$

Selection Rules:

$$\epsilon_1 = -\frac{1}{\sqrt{2}} (\hat{\mathbf{e}}_x + i\hat{\mathbf{e}}_y), \quad \epsilon_0 = \hat{\mathbf{e}}_z, \quad \epsilon_{-1} = \frac{1}{\sqrt{2}} (\hat{\mathbf{e}}_x - i\hat{\mathbf{e}}_y)$$

Photons with $\epsilon_{\pm 1}$ (left/right) have angular momentum of $\pm \hbar$,

photons of ϵ_0 have no angular momentum. Also we write:

$$\begin{aligned} [r_1, r_0, r_{-1}] &= \left[-\frac{1}{\sqrt{2}}(x + iy), z, \frac{1}{\sqrt{2}}(x - iy) \right] \\ &= r \left(\frac{4\pi}{3} \right)^{1/2} [Y_{1,1}(\theta, \varphi), Y_{1,0}(\theta, \varphi), Y_{1,-1}(\theta, \varphi)] \end{aligned}$$

So: $\hat{\mathbf{e}} \cdot \mathbf{r}_{ba} = \sum \epsilon_q^* (\mathbf{r}_{ba})_q = \sum \epsilon_q^* I_{n'\ell'm', n\ell m}^q$

With: $I_{n'\ell'm', n\ell m}^q = \left(\frac{4\pi}{3} \right)^{1/2} \mathcal{A}_{(\ell, m; \ell', m'; q)} \int_0^\infty dr R_{n'\ell'}(r) r^3 R_{n\ell}(r)$

$$\mathcal{A}(\ell', m'; \ell, m; q) = \int d\Omega Y_{\ell'm'}^*(\theta, \varphi) Y_{1q}(\theta, \varphi) Y_{\ell m}(\theta, \varphi)$$

The radial integral is generally non-zero, and the angular integral is non-zero only for $m' - m = q$ and $\ell' - \ell = \pm 1$.

Complex atoms: $\Delta F, \Delta M_F = 0, \pm 1$ but $F = 0 \not\leftrightarrow F' = 0$,

where J is total angular momentum (nucleus + electron + spin).

Energy shift due to magnetic field: $\Delta E = -\boldsymbol{\mu} \cdot \mathbf{B} = g_F \mu_B m B$.

Atomic Units $m_e = q_e = a_0 = \hbar = 4\pi\epsilon_0 = E_h = 1$

Scales: mass m_e , length a_0 , energy E_h , velocity $a_0 E_h / \hbar$,

ang. momentum \hbar . $E_0 = \frac{E_h}{2} = \frac{e^4 m_e}{2\hbar^2} = \frac{\alpha^2 c^2 m_e}{2} = 13.6 \text{ eV}$

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137}, \quad a_0 = \frac{\hbar^2}{m_e e^2} = 0.529 \text{ \AA}$$

One Electron Atoms

Schrödinger's equation:

$$\left[-\frac{\hbar^2}{2\mu} \nabla^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \right] \psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Energy levels: $E_n = -\frac{E_h}{2} \frac{Z^2}{n^2} = -\frac{1}{2} \frac{Z^2}{n^2} = -13.6\text{eV} \frac{Z^2}{n^2}$

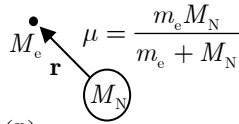
Eigenfunctions $\psi_{n\ell m}(\mathbf{r}) = R_{n\ell}(r) Y_{\ell m}(\theta, \varphi)$ with $R_{n\ell}(r)$:

$$\left\{ -\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) - \frac{\ell(\ell+1)}{r^2} \right] - \frac{Ze^2}{4\pi\epsilon_0 r} - E \right\} R_{n\ell}(r) = 0$$

$$R_{10}(r) = 2(Z/a_0)^{3/2} \exp(-Zr/a_0)$$

$$R_{20}(r) = 2(Z/2a_0)^{3/2} (1 - Zr/2a_0) \exp(-Zr/2a_0)$$

$$R_{21}(r) = (1/\sqrt{3})(Z/2a_0)^{3/2} (Zr/a_0) \exp(-Zr/2a_0)$$



Two Electron Atoms (1/3)

$$H = -\frac{\hbar^2}{2\mu} \nabla_1^2 - \frac{\hbar^2}{2\mu} \nabla_2^2 - \frac{\hbar^2}{M_N} \nabla_1 \cdot \nabla_2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_1} - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_2} + \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{12}} \quad \mu = \frac{m_e M_N}{m_e + M_N}$$

For $M_N \rightarrow \infty$, $\nabla_1 \cdot \nabla_2$ term vanishes and $\mu \cong m_e$.

State Symmetry:

Fermions: $\Psi(q_1, q_2) = -\Psi(q_2, q_1)$.

Overall state $\Psi(q_1, q_2) = \psi(\mathbf{r}_1, \mathbf{r}_2) \chi(1, 2)$ with...

Para-state:	Ortho-states:
$\psi_+(\mathbf{r}_1, \mathbf{r}_2) = +\psi_+(\mathbf{r}_2, \mathbf{r}_1)$	$\psi_-(\mathbf{r}_1, \mathbf{r}_2) = -\psi_-(\mathbf{r}_2, \mathbf{r}_1)$
$\chi(1, 2) = (\uparrow\downarrow\rangle - \downarrow\uparrow\rangle) / \sqrt{2}$	$\chi_{1,1} = \uparrow\uparrow\rangle \quad \chi_{1,-1} = \downarrow\downarrow\rangle$
	$\chi_{1,0} = (\uparrow\downarrow\rangle + \downarrow\uparrow\rangle) / \sqrt{2}$

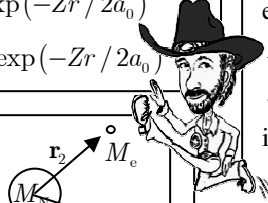
Proving Spatial Parity: Define permutation operator P_{12} & operate on $H_{12}\Psi_{12} = E_{12}\Psi_{12}$, argue that $\Psi_{21} = \lambda\Psi_{12}$ due to non-degeneracy, switch indices $1 \leftrightarrow 2$ and use P_{12} again, and use $H_{12} = H_{21}$ to show $\Psi_{12} = \lambda^2\Psi_{12}$.

Level Scheme of Two Electron Atoms:

Neglecting spin-orbit interactions (valid up to $Z \simeq 40$), radiative transitions between para- and ortho-states are forbidden, so energy spectrum is made of two nearly independent system of levels, para and ortho.

A two-electron atom state is bound if its energy is lower than $E_0(\text{He}^+) = -54.4\text{eV} = -2 \text{ a.u.}$, and the only bound states are singly-excited, $1s, n\ell$. For $Z = 1$ there is in fact only one bound state, $1s^2$.

Singly excited states are written as $n^{2S+1}L$, with S the total spin of the two electrons ($S = 0, 1$) and L their total angular momentum. Para: n^1L and ortho: n^3L .



Two Electron Atoms (2/3)

Independent Particle Model:

Ignoring interaction, $E_{n_1 n_2}^{(0)} = (-Z^2/2)(n_1^{-2} + n_2^{-2})$ with:

$$\psi_{\pm}^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\psi_{n_1 \ell_1 m_1}(\mathbf{r}_1) \psi_{n_2 \ell_2 m_2}(\mathbf{r}_2) \pm \psi_{n_2 \ell_2 m_2}(\mathbf{r}_1) \psi_{n_1 \ell_1 m_1}(\mathbf{r}_2)]$$

Exchange-degeneracy removed by interaction term. Singly-excited levels $n^{2S+1}L$ have energies $E_n^{(0)} = (-Z^2/2)(1 + n^{-2})$.

Screening:

Improve independent model by using an effective $Z_{\text{eff}} = Z - S$ to simulate screening. Even better to have screening vary with r with $S_{(r \rightarrow 0)} = 0$ and $S_{(r \rightarrow \infty)} = 1$. This is not Coulomb potential so the energy depends on ℓ , now the excited bound states have energies

$\tilde{E}_{1s, n\ell}^{(0)} = E_{1s} + E_{n\ell}$. Lower ℓ means lower centrifugal barrier

$\ell(\ell+1)/r^2$, thus the electron feels less screening, so $E_{n\ell}$ increases with ℓ and this removes degeneracy of $n^{2S+1}L$ in L .

Exchange Force:

Ortho-states ($-$) vanish for $\mathbf{r}_1 = \mathbf{r}_2$ while para-states ($+$) don't necessarily, so interaction term $1/r_{12}$ will raise the para-states more than the ortho-states. Generally: $E(n^1L) > E(n^3L)$.

As n increases the overlap between the electrons diminishes so the exchange term becomes less significant.

The Ground State - Perturbation:

Is a singlet, space-symmetric state: $\Psi_0(q_1, q_2) = \psi_0(\mathbf{r}_1, \mathbf{r}_2) \chi_{00}(1, 2)$.

First-order perturbation theory for the $1/r_{12}$ term gives a correction:

$$E_0^{(1)} = \langle \Psi_0^{(0)} | 1/r_{12} | \Psi_0^{(0)} \rangle = \int |\psi_{1s}(r_1)|^2 \frac{1}{r_{12}} |\psi_{1s}(r_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 = 5Z/8$$

So the first-order ground state energy is $E_0 = -Z^2 + 5Z/8$, with the correction $|E_0^{(1)}/E_0^{(0)}| \sim Z^{-1}$ as expected. (Z^{-1} is "small parameter")

The Ground State - Variational:

Use an effective Z_{eff} for the Hydrogenic wavefunction, but keep the original Hamiltonian (with Z), and find Z_{eff} that minimizes

$$E[\Psi_0^{Z_{\text{eff}}}] = \langle \Psi_0^{Z_{\text{eff}}} | H | \Psi_0^{Z_{\text{eff}}} \rangle / \langle \Psi_0^{Z_{\text{eff}}} | \Psi_0^{Z_{\text{eff}}} \rangle$$

This gives $Z_{\text{eff}} = Z - 5/16$ for so $E_0 = -(Z - 5/16)^2$, which is lower and in better agreement with experiments than perturbative result.

The Ground State - Further corrections:

Corrections for a finite M_N introduce a scale of the energies by μ/m_e or $M_N/(m_e + M_N)$, and also a correction from the $\nabla_1 \cdot \nabla_2$ term. The latter vanishes for the ground state if both electrons are in spherical states for which $\langle \Psi_0 | \nabla_1 \cdot \nabla_2 | \Psi_0 \rangle = \langle \psi_0 | \nabla_1 | \psi_0 \rangle \cdot \langle \psi_0 | \nabla_2 | \psi_0 \rangle = 0$ since the average radial momentum of a spherical wave is zero.

Trigonometric Identities, Legendre Polynomials & Spherical Harmonics

$$\sin(\alpha \pm \beta) = \sin \alpha \cos \beta \pm \cos \alpha \sin \beta$$

$$\tan(\alpha \pm \beta) = \frac{\tan \alpha \pm \tan \beta}{1 \mp \tan \alpha \tan \beta}$$

$$\sin \alpha + \sin \beta = 2 \sin \left(\frac{\alpha + \beta}{2} \right) \cos \left(\frac{\alpha - \beta}{2} \right)$$

$$\sin \alpha \sin \beta = \frac{1}{2} [\cos(\alpha - \beta) - \cos(\alpha + \beta)]$$

$$\int_{-1}^1 P_{\ell'}^m(x) P_{\ell}^m(x) dx = \frac{2}{2\ell + 1} \frac{(\ell + m)!}{(\ell - m)!} \delta_{\ell, \ell'}$$

$$(2\ell + 1)x P_{\ell}^m(x) = (\ell + 1 - m) P_{\ell+1}^m(x) + (\ell + m) P_{\ell-1}^m(x)$$

$$(2\ell + 1)\sqrt{1-x^2} P_{\ell}^{m-1}(x) = P_{\ell+1}^m(x) - P_{\ell-1}^m(x)$$

$$P_{\ell}^{(-m)} = (-1)^m \frac{(\ell - m)!}{(\ell + m)!} P_{\ell}^{(m)}, \quad P_{-\ell}^{(m)} = P_{\ell-1}^{(m)}$$

$$P_0^0(x) = 1, \quad P_1^0(x) = x, \quad P_1^1(x) = -\sqrt{1-x^2}$$

$$Y_{\ell m}(\theta, \varphi) = \sqrt{\frac{2\ell + 1}{4\pi} \frac{(\ell - m)!}{(\ell + m)!}} P_{\ell}^m(\cos \theta) e^{im\varphi}$$

$$\int_{4\pi} Y_{\ell' m'}^*(\theta, \varphi) Y_{\ell m}(\theta, \varphi) d\Omega = \delta_{\ell, \ell'} \delta_{m, m'}$$

$$Y_{\ell m}^*(\theta, \varphi) = (-1)^m Y_{\ell, -m}(\theta, \varphi)$$

$$x = r \left(\frac{2\pi}{3} \right)^{1/2} [Y_{1,-1}(\theta, \varphi) - Y_{1,1}(\theta, \varphi)]$$

$$y = r \left(\frac{2\pi}{3} \right)^{1/2} [iY_{1,-1}(\theta, \varphi) + iY_{1,1}(\theta, \varphi)]$$

$$z = r \left(\frac{4\pi}{3} \right)^{1/2} Y_{1,0}(\theta, \varphi)$$

Many Electron Atoms (1/2)

$$\left[\sum_{i=1}^N \left(-\frac{1}{2} \nabla_{\mathbf{r}_i}^2 - \frac{Z}{r_i} \right) + \sum_{i < j=1}^N \frac{1}{r_{ij}} \right] \Psi(q_1, \dots, q_N) = E \Psi$$

Repulsion terms $1/r_{ij}$ not small as in two-electron atom so can't use them as perturbation.

We define an effective central field potential:

$$V(r) = -Z/r + S(r) = \begin{cases} -\frac{Z}{r} & r \rightarrow 0 \\ -\frac{Z - N + 1}{r} & r \rightarrow \infty \end{cases}$$

So $H' = \sum_{i < j=1}^N \frac{1}{r_{ij}} - \sum_{i=1}^N S(r_i)$ is a small perturbation.

Potential is radial so wavefunction of each electron is $u_{n\ell m_\ell m_s}(\mathbf{r}) = R_{n\ell}(r) Y_{\ell m_\ell}(\theta, \varphi) \chi_{\frac{1}{2} m_s}$, where the energy is $E = E_{n\ell}$ and depends on ℓ because the potential is more complex than simple Coulomb.

Slater Determinants:

Given N electrons occupying the different states $u_\alpha(q), u_\beta(q), \dots, u_\nu(q)$, the determinant

$$\Psi_{\text{SD}} = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_\alpha(q_1) & u_\beta(q_1) & \dots & u_\nu(q_1) \\ u_\alpha(q_2) & u_\beta(q_2) & \dots & u_\nu(q_2) \\ \vdots & \vdots & \ddots & \vdots \\ u_\alpha(q_N) & u_\beta(q_N) & \dots & u_\nu(q_N) \end{vmatrix}$$

gives an anti-symmetric state that satisfies Pauli's exclusion principle. Can also be written as:

$$\Psi_{\text{SD}} = \frac{1}{\sqrt{N!}} \sum_P (-1)^{N(P)} P[u_\alpha(q_1) \dots u_\nu(q_N)]$$

Sum over all possible permutations and $N(P)$ is the number of interchanges of each permutation.

If the individual orbitals $u_i(q_i)$ have parity ℓ_i ,

the determinant has parity $\sum_{i=1}^N \ell_i$.

Slater determinant is made of states with definite m_ℓ and m_s so it is eigenstate of L_z and S_z , but not necessarily of \mathbf{L}^2 and \mathbf{S}^2 . In order to find do that, we must use a linear combination of determinants, changing the m_ℓ and m_s values of the inner states (which is okay since they don't affect the energy).

Qualitative Energy Levels:

Generally $E = E_{n\ell}$ increases with n and ℓ (separately), since higher n, ℓ means larger orbitals and more screening of nucleus. Generally the order of energy levels is:

$1s, 2s, 2p, 3s, 3p, [4s, 3d], 4p, [5s, 4d], 5p, [6s, 4f, 5d], 6p, [7s, 5f, 6d]$
(bracketed levels are very near and can vary in order)

The alkali metals (Li, Na, K, Rb, Cs) have one electron in outer shell which sees a lot of screening so the ionization potential I_p is very low. The next atoms have more electrons in the outer shell but they barely screen each other, so I_p increases due to higher nucleus attraction. The noble gases (He, Ne, Ar, Kr, Xe) have highest I_p because they have full outer shells.

Configuration Degeneracy:

Each sub-shell (n, ℓ) is degenerate $2\ell(\ell + 1)$ times. The number of configurations of ν electrons in the n, ℓ sub-shell is given by $d = \delta! / \nu! (\delta - \nu)!$, with $\delta = 2\ell(\ell + 1)$. The total degeneracy of an atom is given by the sum of d 's for its occupied sub-shells.

Two Electron Atoms (3/3)

Bound Excited States – Perturbation:

Zero-order states: $\psi_{\pm}^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\psi_{100}(\mathbf{r}_1) \psi_{n\ell m}(\mathbf{r}_2) \pm \psi_{n\ell m}(\mathbf{r}_1) \psi_{100}(\mathbf{r}_2)]$

Perturbation $H' = 1/r_{12}$ is diagonal in the degenerate zero-order wavefunctions (same n with different ℓ, m vanishes by spherical harmonics, $\psi_{\pm}^{(0)}$ and $\psi_{\mp}^{(0)}$ with same n vanishes from $1 \leftrightarrow 2$ symmetry).

The correction is then simply $E_{n\ell, \pm}^{(1)} = \langle \psi_{\pm}^{(0)} | H' | \psi_{\pm}^{(0)} \rangle = J_{n\ell} \pm K_{n\ell}$ with

$$J_{n\ell} = \int |\psi_{100}(\mathbf{r}_1)|^2 \frac{1}{r_{12}} |\psi_{n\ell m}(\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 = \int_0^\infty dr_2 r_2^2 R_{n\ell}^2(r_2) \int_0^\infty dr_1 r_1^2 R_{10}^2(r_1) \frac{1}{r_{>}}$$

$$K_{n\ell} = \int \psi_{100}(\mathbf{r}_1) \psi_{n\ell m}^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_{100}(\mathbf{r}_2) \psi_{n\ell m}(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2$$

$$= \frac{1}{2\ell + 1} \int_0^\infty dr_2 r_2^2 R_{10}(r_2) R_{n\ell}(r_2) \int_0^\infty dr_1 r_1^2 R_{10}(r_1) R_{n\ell}(r_1) \frac{r_{<}}{r_{>}^{\ell+1}}$$

These are the direct (Coulomb) and exchange integrals, which are independent of m since $[H', L_z] = 0$. The energy levels are thus

$$E_{n\ell, \pm} = -\frac{Z^2}{2} \left(1 + \frac{1}{n^2} \right) + J_{n\ell} \pm K_{n\ell} \text{ and generally } J_{n\ell}, K_{n\ell} > 0 \text{ so that}$$

$E_{n\ell, +} > E_{n\ell, -}$; the para-state (singlet) has higher energy than the ortho-states (triplet). This completely splits between the $2^1S, 2^3S, 2^1P$ and 2^3P states.

Bound Excited States – Variational:

Find state ϕ with minimal $E[\phi] = \langle \phi | H | \phi \rangle / \langle \phi | \phi \rangle$ and also orthogonal to all lower states. The excited state 2^3S is ortho ($-$) and so orthogonal to the para ($+$) ground state 1^1S . Guessing a wavefunction

$$\phi_{2^3S}(\mathbf{r}_1, \mathbf{r}_2; Z_{\text{in}}, Z_{\text{out}}) = u_{1s}(\mathbf{r}_1, Z_{\text{in}}) u_{2s}(\mathbf{r}_2, Z_{\text{out}}) - u_{2s}(\mathbf{r}_1, Z_{\text{out}}) u_{1s}(\mathbf{r}_2, Z_{\text{in}})$$

gives $Z_{\text{in}} = 2.01, Z_{\text{out}} = 1.53$ which shows screening of the outer electron.

The excited states 2^1P and 2^3P have $L = \ell = 1$ are also orthogonal to both 1^1S and 2^3S (2^1S is higher so doesn't matter) so we propose:

$$\phi_{2^{1,3}P}(\mathbf{r}_1, \mathbf{r}_2; Z_{\text{in}}, Z_{\text{out}}) = u_{1s}(\mathbf{r}_1, Z_{\text{in}}) u_{2p_m}(\mathbf{r}_2, Z_{\text{out}}) \pm u_{2p_m}(\mathbf{r}_1, Z_{\text{out}}) u_{1s}(\mathbf{r}_2, Z_{\text{in}})$$

and obtain $Z_{\text{in}}^{2^1P} = 2.00, Z_{\text{out}}^{2^1P} = 0.97, Z_{\text{in}}^{2^3P} = 1.99$ and $Z_{\text{out}}^{2^3P} = 1.09$.

Doubly Excited States:

The autoionising states are in the continuum, and couple to the continuum states via the interaction $1/r_{12}$. This results in radiationless transitions, (Auger effect) that are more probable than radiative transitions to lower states. The absorption spectrum shows sharp peaks near the autoionising states, since they improve the probability of radiation absorption.

Fermi Electron Gas

Energy of a particle in a large 3D box is $E = \pi^2 \hbar^2 n^2 / 2mL$ where $n^2 = n_x^2 + n_y^2 + n_z^2$. The number of states N_s is given by $2 \cdot \frac{1}{8} \cdot (4\pi n_F^3 / 3)$ or in terms of the energy:

$$N_s = \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{VE^{3/2}}{3\pi^2}, \quad D(E) = \frac{dN_s}{dE} = \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{VE^{1/2}}{2\pi^2}$$

The highest occupied energy level E_F is found from

$$N = \int_0^{E_F} D(E) dE \text{ where } N \text{ is the number of particles. This}$$

gives $E_F = \frac{\hbar^2}{2m} (3\pi^2 \rho)^{2/3}$ with $\rho = N/V$.

We also define $k_F = (3\pi^2 \rho)^{1/3}$ since each k -state has volume $V/8\pi^3$. Some more relations:

$$E_F = \frac{\hbar^2}{2m} k_F^2 = \frac{p_F^2}{2m} = \frac{1}{2} m v_F^2 = k T_F$$

Many Electron Atoms (2/2)

Thomas-Fermi Model:

Assume an atom with many electrons bound by a potential $V(r)$, which varies slowly so each electron sees a constant potential, and there are many electrons at the same potential, so they form a free electron gas. Maximum energy of an electron is $E_{\max} = E_F + V(r)$ with $E_{\max} < 0$ independent of r . So

k_F is a function of r thru E_F : $k_F^2(r) = 2m[E_{\max} - V(r)]/\hbar^2$

And the density is thus $\rho(r) = \frac{1}{3\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} [E_{\max} - V(r)]^{3/2}$

with $\rho(r) = 0$ when $V(r) \geq E_{\max}$. We define:

$$\phi(r) = -\frac{1}{e}V(r), \quad \phi_0 = -\frac{E_{\max}}{e} > 0, \quad \Phi(r) = \phi(r) - \phi_0$$

And find equation: $\rho(r) = \begin{cases} \frac{1}{3\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} [e\Phi(r)]^{3/2} & \Phi \geq 0 \\ 0 & \Phi < 0 \end{cases}$

$\Phi(r) = 0$ (or $V(r) = E_{\max}$) defines the boundary of the atom.

Also, Poisson's equation: $\nabla^2\Phi(r) = \frac{1}{r} \frac{d^2}{dr^2} [r\Phi(r)] = \frac{e}{\epsilon_0} \rho(r)$

We scale: $b = \frac{(3\pi)^{2/3}}{2^{7/3}} a_0 Z^{-1/3} \cong 0.8853 a_0 Z^{-1/3}$

$$r = bx, \quad r\Phi(r) = \frac{Ze}{4\pi\epsilon_0} \chi(x)$$

And find the universal problem: $\lim_{x \rightarrow 0} \chi(x) = 1$

$$N = Z \int_0^{x_0} x^{1/2} \chi^{3/2} dx = Z [x\chi' - \chi]_0^{x_0}$$

$$\frac{d^2}{dx^2} \chi(x) = \begin{cases} x^{-1/2} [\chi(x)]^{3/2} & \chi \geq 0 \\ 0 & \chi < 0 \end{cases}$$

The first two equations come from nucleus attraction and the total number of electrons. The normalization equation gives $x_0\chi'(x_0) = (N - Z)/Z$, so for a neutral atom $\chi'(x_0) = 0$.

But there is no such non-trivial solution so $x_0 = \infty$ and there is no sharp boundary. The solution $\chi(x)$ is universal to all

neutral atoms with: $\chi(x) = \begin{cases} 1 - 1.588x + \dots & x \ll 1 \\ 144x^{-3} & x \gg 1 \end{cases}$

So $V(r)$ vanishes as r^{-4} , and faster than r^{-1} (since

$\chi(x) = r\Phi(r) \xrightarrow{r \rightarrow \infty} 0$). In the independent particle model we

assumes $V(r) \xrightarrow{r \rightarrow \infty} -\frac{Z - N + 1}{r} \propto \frac{1}{r}$, but that was a potential

felt by an atomic electron, and here it's the potential felt by an infinitesimal test charge. **Important:** length scale of the solution is $b \sim Z^{-1/3}$, so the atoms contract according to $Z^{-1/3}$.

This model is inaccurate for small distances, $r < a_0/Z$, and diverges at the origin; and at large distances, $r \gg a_0$, where it

overestimates the electron density, which falls like r^{-6} and not exponentially. So this model should only be used for electrons located between a_0/Z to a few a_0 's, but luckily for large

atoms that is where most of them are. So the Thomas-Fermi model gives good results for the "average" electron in large atoms, but poor results for the outer (valence) electrons, such as ionization potential. The state density is $g(\epsilon) = d\rho/d\epsilon$ and

the total kinetic energy: $E_k = (3^{5/3}\pi^{4/3}/10m) \int [\rho(\mathbf{r})]^{5/3} d\mathbf{r}$

Hartree-Fock Method: Independent particle model which finds both ψ and $V(r)$ that match each other, through the algorithm:

1) Guess a wavefunction ψ ; 2) Determine potential $V(r)$ from the wavefunction ψ ; 3) Solve this $V(r)$ for a new ψ ; 4) return to step 2. The result $V(r)$ is called the self-consistent field of the atom.

$$\text{Particle in a Box: } E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2, \quad u_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

Molecular Structure (1/3)

Molecular Energy Scales:

If a is the typical distance of nuclei in molecules, the momentum of the valence electrons is on the order of \hbar/a so their energy is

on the order of $E_e \simeq \hbar^2/ma^2$. The force constant k is identical for nuclei and electrons, but $\omega_e = \sqrt{k/m}$ and $\omega_N = \sqrt{k/M}$ so

the nuclei's vibration energy is on order of $E_v \simeq (\sqrt{m/M}) E_e$.

A diatomic molecule's moment of inertia is $I = Ma^2/2$ so its rotational energy is on order of $E_r \simeq \hbar^2/I \simeq (m/M) E_e$.

So vibration energies are a first order correction to the electronic energies, of order $\sqrt{m/M} \approx 10^1-10^3$, and the rotational energies are a second order correction of order $m/M \approx 10^3-10^5$.

Born-Oppenheimer Separation:

A motion's period is on the order of \hbar/E so the nuclear periods (vibrational and rotational) are slower than the electronic periods. So it is possible to solve the electronic wavefunction for a fixed location of the nuclei, considering them stationary.

The time-independent Schrödinger equation for a diatomic molecule with N electrons is given by:

$$[T_N + T_e + V] \psi(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E \psi(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

where $\mathbf{R} = \mathbf{R}_A - \mathbf{R}_B$ is the relative position of the nuclei, and:

$$T_N = -\frac{\hbar^2}{2\mu} \nabla_{\mathbf{R}}^2, \quad T_e = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 \right), \quad \mu = \frac{M_A M_B}{M_A + M_B}$$

$$V = -\frac{1}{4\pi\epsilon_0} \sum_{i=1}^N \frac{Z_A e^2}{|\mathbf{r}_i - \mathbf{R}_A|} - \frac{1}{4\pi\epsilon_0} \sum_{i=1}^N \frac{Z_B e^2}{|\mathbf{r}_i - \mathbf{R}_B|} + \frac{1}{4\pi\epsilon_0} \sum_{i>j=1}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{4\pi\epsilon_0} \sum_{i=1}^N \frac{Z_A Z_B e^2}{R}$$

The time-independent Schrödinger equation for the electrons moving around the fixed nuclei at \mathbf{R}_A and \mathbf{R}_B (\mathbf{R}) is given by

$$[T_e + V] \Phi_s(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E_s \Phi_s(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

where s denotes a state. This is the **electronic wave equation** and it is solved parametrically for every value of \mathbf{R} . The set of wavefunctions $\{\Phi_s\}$ form a complete set for every \mathbf{R} and the

exact wavefunction ψ for the molecule can then be expanded as

$$\psi(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_s F_s(\mathbf{R}) \Phi_s(\mathbf{R}; \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

The coefficients $F_s(\mathbf{R})$ are given by the coupled equations

$$\sum_q \left[\int d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \Phi_s^* T_N \Phi_q F_q(\mathbf{R}) \right] + [E_s(\mathbf{R}) - E] F_s(\mathbf{R}) = 0$$

for $s = 1, 2, \dots$. These are uncoupled by the Born-Oppenheimer approximation: writing T_N explicitly, assume $|\nabla_{\mathbf{R}} \Phi_s| \ll |\nabla_{\mathbf{R}} F_s|$ near the equilibrium point R_0 and then the **nuclear wave equation**

$$\text{is: } \left[-\frac{\hbar^2}{2\mu} \nabla_{\mathbf{R}}^2 + E_s(\mathbf{R}) \right] F_s(\mathbf{R}) = E F_s(\mathbf{R})$$

The approximation due to the fact that the nuclei are very much localized at the center of the molecule, and the electrons much less so, so the space derivative of F_s dominates than that of Φ_s .

Molecular Structure (2/3)

Symmetry Properties of Diatomic Molecules:

Electronic molecular Hamiltonian $H_e = T_e + V$ commutes with L_z but not L_x, L_y or L^2 . So we have for the electronic states Φ_s :
 $L_z \Phi_s = M_L \hbar \Phi_s = \pm \Lambda \hbar \Phi_s$, $M_L = 0, \pm 1, \pm 2, \dots$, $\Lambda = |M_L|$
 H_e is also invariant for reflections in planes containing Z axis, for example A_y , a reflection through the XZ axis ($y_i \rightarrow -y_i$). We have $[H, A_y] = 0$ and $A_y L_z = -L_z A_y$ so operating with A_y on Φ_s with eigenvalue $\Lambda \hbar$ for L_z creates a wavefunction with eigenvalue $-\Lambda \hbar$ with the same energy, so states with $\Lambda \neq 0$ are doubly-degenerate. For $\Lambda = 0$, $A_y \Phi_{\Lambda=0}$ can differ from $\Phi_{\Lambda=0}$ only by a constant, and $A_y^2 = 1$ so $A_y \Phi_{\Lambda=0} = \pm \Phi_{\Lambda=0}$. So we have Σ^\pm states for which $A_y \Sigma^\pm = \pm \Sigma^\pm$.

Homonuclear molecules are also invariant under inversion $\mathbf{r}_i \rightarrow -\mathbf{r}_i$ so their wavefunction must have well defined space parity. Symmetric states are called gerade and anti-symmetric are called ungerade, so we have $\Sigma_g, \Sigma_u, \Pi_g, \Pi_u, \dots$ etc. For homonuclear diatomic molecules there are four non-degenerate Σ states: $\Sigma_g^+, \Sigma_g^-, \Sigma_u^+, \Sigma_u^-$. Another symmetry is changing $\mathbf{R} \rightarrow -\mathbf{R}$ (without changing \mathbf{r}_i 's), which can be done by a rotation of the whole system a 180° about the Y axis, then reflecting $y_i \rightarrow -y_i$ and inverting $\mathbf{r}_i \rightarrow -\mathbf{r}_i$. The first rotation changes nothing, and the two reflections leave the Σ_g^+ and Σ_u^- states unchanged, but change the sign of Σ_u^+ and Σ_g^- .

Spectroscopic Notation:

Electronic states are $^{2S+1}\Lambda_{g/u}^{+/-}$ where S is the total spin of the electrons and $\Lambda = \Sigma, \Pi, \Delta, \dots$ is the L_z eigenvalue. The ground state has X in front of it; a non-binding state has $*$ above it.

The von Neumann-Wigner Non-Crossing Rule:

Let $E_1(R)$ and $E_2(R)$ be two electronic potential curves, that come close at R_c but don't quite intersect, with corresponding orthonormal electronic states $\Phi_1^{(0)}$ and $\Phi_2^{(0)}$. Is there some ΔR such that at $R = R_c + \Delta R$ the potential curves intersect?

Define $H(R_c + \Delta R) = H(R_c) + \Delta H$, $\Delta H = \Delta R \cdot \partial H / \partial R_c$, and $\Delta H_{ij} = \langle \Phi_i^{(0)} | \Delta H | \Phi_j^{(0)} \rangle$. From perturbation theory, for the curves to intersect we need to have ΔR satisfy two equations:

$$E_2^{(0)} - E_1^{(0)} = \Delta H_{11} - \Delta H_{22}, \quad \Delta H_{12} = 0$$

If $\Phi_1^{(0)}$ and $\Phi_2^{(0)}$ have different symmetries, ΔH_{12} vanishes for all ΔR (because H commutes with the symmetry operators) so it is possible to find a specific ΔR to satisfy the first equation and we will see crossing. However if the states have the same symmetries (all of them), ΔH_{12} will generally be non-zero and we won't be able to find a single ΔR to satisfy both equations (except for coincidences) and there will generally be no crossing.

Hydrogen Molecular Ion H_2^+ - LCAO Method:

The electronic wave equation in atomic units is given by:

$$\left(-\frac{1}{2} \nabla_r^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) \Phi_s(\mathbf{R}; \mathbf{r}) = E_s \Phi_s(\mathbf{R}; \mathbf{r})$$

where $\mathbf{r}_A = \mathbf{r} + \mathbf{R}/2$ and $\mathbf{r}_B = \mathbf{r} - \mathbf{R}/2$, \mathbf{r} is the position of the electron with respect to the midpoint between the nuclei. For the molecule's ground state, we will assume that the electron is in the atomic ground state $\psi_{1s}(r) = \pi^{-1/2} \exp(-r)$ and construct symmetric electronic wave functions as such:

$$\Phi_{g,u}(\mathbf{R}; \mathbf{r}) = \frac{1}{\sqrt{2}} [\psi_{1s}(r_A) \pm \psi_{1s}(r_B)]$$

This is the linear combination of atomic orbitals (LCAO) method. The energies $E(R) = \langle \Phi | H | \Phi \rangle / \langle \Phi | \Phi \rangle$ are:

$$E_{g,u}(R) = E_{1s} + \frac{1}{R} \frac{(1+R)e^{-2R} \pm (1-2R^2/3)e^{-R}}{1 \pm (1+R+R^2/3)e^{-R}}$$

Where $E_{1s} = -0.5$ a.u is the limit as $R \rightarrow \infty$ which makes sense. $E_g(R)$ has a minimum and is a bonding state $\sigma_g 1s$;

$E_u(R)$ is purely repulsive and is thus antibonding state $\sigma_u^* 1s$. The charge density $\rho_g = -e|\Phi_g|^2$ has an excess negative charge between the nuclei (compared to the sum of densities of two half-electron atoms) which causes the binding; the density $\rho_u = -e|\Phi_u|^2$ has a deficiency of negative charge between the nuclei (even vanishes at middle) so their repulsion dominates.

Molecular Hydrogen H_2 - Molecular Orbital Method:

The electronic Hamiltonian in atomic units is given by:

$$H = \sum_{i=1}^2 H_0(i) + \left(\frac{1}{r_{12}} + \frac{1}{R} \right), \quad H_0(i) = -\frac{1}{2} \nabla_{r_i}^2 - \frac{1}{r_{A_i}} - \frac{1}{r_{B_i}}$$

The six possibilities for an electronic state of definite S are:

$$^1\Sigma_g^+ : \Phi_A(1,2) = \Phi_g(1)\Phi_g(2)\chi_{0,0}(1,2)$$

$$^1\Sigma_g^+ : \Phi_B(1,2) = \Phi_u(1)\Phi_u(2)\chi_{0,0}(1,2)$$

$$^1\Sigma_u^+ : \Phi_C(1,2) = \frac{1}{\sqrt{2}} [\Phi_g(1)\Phi_u(2) + \Phi_u(1)\Phi_g(2)]\chi_{0,0}(1,2)$$

$$^3\Sigma_u^+ : \Phi_D(1,2) = \frac{1}{\sqrt{2}} [\Phi_g(1)\Phi_u(2) - \Phi_u(1)\Phi_g(2)]\chi_{1,M_S}(1,2)$$

Φ_A is expected to have the lowest energy, which is:

$$E_A(R) = 2E_g(R) - \frac{1}{R} + \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{|\Phi_g(1)\Phi_g(2)|^2}{r_{12}}$$

In evaluating this we can use the 'exact' Φ_g molecular orbital or the approximate one we obtained earlier, both for H_2^+ .

Φ_A can also be written as $\Phi_A = \Phi_A^{\text{cov}} + \Phi_A^{\text{ion}}$ where:

$$\Phi_A^{\text{cov}} = \frac{1}{2} [\psi_{1s}(r_{A1})\psi_{1s}(r_{B2}) + \psi_{1s}(r_{A2})\psi_{1s}(r_{B1})]\chi_{0,0}(1,2)$$

$$\Phi_A^{\text{ion}} = \frac{1}{2} [\psi_{1s}(r_{A1})\psi_{1s}(r_{A2}) + \psi_{1s}(r_{B1})\psi_{1s}(r_{B2})]\chi_{0,0}(1,2)$$

Φ_A^{cov} represents covalent bonding, each electron is associated to another nucleus; Φ_A^{ion} is ionic bonding, both electrons are at one nucleus. Φ_A^{ion} is not a good depiction of molecular Hydrogen so Φ_A in general is not a very good approx. So a mixed orbital is proposed: $\Phi_T = \Phi_A + \lambda \Phi_B = (1-\lambda)\Phi_A^{\text{cov}} + (1+\lambda)\Phi_A^{\text{ion}}$ for which we calculate $E(R; \lambda)$ and minimize it with respect to both variables. We can also define $q = (1+\lambda)/(1-\lambda)$ which is the ratio of ionic to covalent part in the wave function.

Molecular Hydrogen H_2 - Valence Bond Method:

(Heitler and London method) Use atomic orbitals, not molecular, where each nucleus has one electron. The two possibilities are:

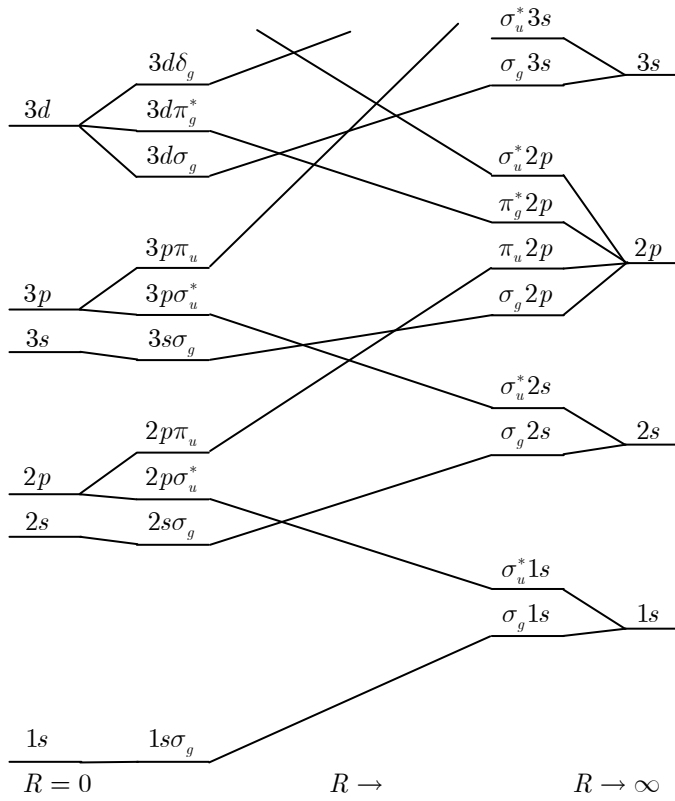
$$^1\Sigma_g^+ : \Phi_+ = \frac{1}{\sqrt{2}} [\psi_{1s}(r_{A1})\psi_{1s}(r_{B2}) + \psi_{1s}(r_{A2})\psi_{1s}(r_{B1})]\chi(1,2)$$

$$^3\Sigma_u^+ : \Phi_- = \frac{1}{\sqrt{2}} [\psi_{1s}(r_{A1})\psi_{1s}(r_{B2}) - \psi_{1s}(r_{A2})\psi_{1s}(r_{B1})]\chi(1,2)$$

But actually $\Phi_+ = \Phi_A^{\text{cov}}$ and $\Phi_- = \Phi_D^{\text{cov}} = \Phi_D$, so this method, appropriately named, takes into account valence bonding only.

Molecular Structure (3/3)

Many Electron Homonuclear Diatomic Molecules:



Correspondence is made so that: 1) MOs having the same λ (i.e. σ, π, \dots) connect with atomic orbitals with the same λ , i.e. same $|m|$; 2) The parity of a state (g/u) is preserved; 3) Energies of states with same symmetry do not cross (von Neuman-Wigner). An MO contains two electrons. For example He_2 has 8 electrons total, with a configuration $(\sigma_g 1s)^2 (\sigma_u^* 1s)^2$, which is not quite stable. Carbon has 6 electrons as $1s^2 2s^2 2p^2$ so the MOs are $[(\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2] (\sigma_g 2p)^2 (\pi_u 2p)^2$. The first four have little net effect, the last two are bonding and so is the state.

Vibrational and Rotational Energies:

Near the equil. point R_0 the electronic potential $E_s(R)$ can be expanded to 2nd order, vibration energies are $E_v = \hbar\omega_0(\nu + 1/2)$

with the frequency given by: $\omega_0 = \sqrt{\frac{k_s}{\mu}} = \sqrt{\frac{1}{\mu} \frac{d^2 E_s}{dR^2}} \Big|_{R_0}$

For molecular orbits where the electrons have non-zero angular momentum \mathbf{L} (not Σ states) and the nuclei have angular momentum \mathbf{N} , define $\mathbf{K} = \mathbf{N} + \mathbf{L}$. Since $\mathbf{N} = \mathbf{R} \times \mathbf{P}_N$ we have $\mathbf{N} \cdot \mathbf{R} = 0$ so that $L_z = K_z$ ($\mathbf{R} \propto \hat{z}$). We work in eigenstates of L_z and so also of K_z , therefore the expectation value of L_x and L_y vanish so that $\langle \mathbf{K} \cdot \mathbf{L} \rangle = \langle K_z L_z \rangle = \Lambda^2 \hbar^2$ and we can write:

$$\langle \mathbf{N}^2 \rangle = \langle (\mathbf{K} - \mathbf{L})^2 \rangle = \hbar^2 K(K+1) - \Lambda^2 \hbar^2 + \langle L_x^2 + L_y^2 \rangle$$

Last two terms depend on the electronic state and can be included in $E_s(R)$: $E'_s(R) = E_s(R) + \frac{1}{2\mu R^2} (\langle L_x^2 + L_y^2 \rangle - \Lambda^2 \hbar^2)$

and in fact they are generally small compared with $E_s(R)$ since $\mu \gg m_e$ and so can be neglected. Thus the added energy due to

rotation is: $E_r = \frac{\langle \mathbf{N}^2 \rangle}{2\mu R_0^2} \approx \frac{\hbar^2 K(K+1)}{2\mu R_0^2} = BK(K+1)$

The actual dissociation energy D_0 of a molecule is D_e , the minimal electronic potential, plus any rovibronic energies.

Scattering of Particles and Atoms

General Definitions:

For potentials that vanish faster than r^{-1} we write away from the collision the wavefunction of the system as the sum:

$$\psi_{\mathbf{k}}(\mathbf{r}) \underset{r \rightarrow \infty}{\sim} \psi_{\text{inc}}(\mathbf{r}) + \psi_{\text{sc}}(\mathbf{r})$$

$$\psi_{\text{inc}}(\mathbf{r}) = A \exp(ikz), \quad \psi_{\text{sc}}(\mathbf{r}) = Af(k, \theta) e^{ikr}/r$$

$E^2 = \hbar^2 k^2 / 2\mu$ is the energy of incident particles. $f(k, \theta)$ is the scattering amplitude and is independent of ϕ because for spherical potentials. The radial current is given at large r by:

$$\mathbf{j}_{\text{sc}} \cdot \hat{\mathbf{r}} = \frac{\hbar}{2mi} \left(\psi_{\text{sc}}^* \frac{\partial \psi_{\text{sc}}}{\partial r} - \frac{\partial \psi_{\text{sc}}^*}{\partial r} \psi_{\text{sc}} \right) = |A|^2 v |f(k, \theta)|^2 / r^2$$

Neglecting terms of higher order in r^{-1} . The outgoing flux per unit solid angle is $j_{\text{sc}} r^2 d\Omega$, the incoming flux is $|A|^2 v$, so the differential cross section is:

$$d\sigma = |f(k, \theta)|^2 d\Omega$$

For bosons and fermions the wavefunction has to be

symmetrized: $\psi_{\pm}(\mathbf{r}) = A [f(k, \theta) \pm f(k, \pi - \theta)] \frac{e^{ikr}}{r}$

So for them we have: $d\sigma = |f(k, \theta) \pm f(k, \pi - \theta)|^2 d\Omega$

Conservation of probability flux: $r^2 \int (\mathbf{j}_{\text{inc}} + \mathbf{j}_{\text{sc}}) \cdot \hat{\mathbf{r}} d\Omega = 0$

Gives the optical theorem: $\sigma_{\text{total}} = \frac{4\pi}{k} \text{Im} f(k, \theta = 0)$

Method of Partial Waves:

$$f(k, \theta) = \frac{1}{k} \sum_{\ell=0}^{\infty} (2\ell+1) e^{i\delta_{\ell}(k)} \sin[\delta_{\ell}(k)] P_{\ell}(\cos \theta)$$

δ_{ℓ} are determined by the asymptotic behavior of the scattered wavefunction, which generally has the form:

$$R_{\ell}(k, r) = \frac{u_{\ell}(k, r)}{r} \underset{r \rightarrow \infty}{\sim} \frac{A_{\ell}(k)}{kr} \sin[kr - \ell\pi/2 + \delta_{\ell}(k)]$$

With $u_{\ell}(k, r)$ being the solution to the radial equation:

$$\left[\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} - U(r) + k^2 \right] u_{\ell}(k, r) = 0$$

where the potential is $(2\mu/\hbar^2)V(r)$. $u_{\ell}(k, r)$ is continuous and $u'_{\ell}(k, r)$ as well, except for singular potentials when:

$$u'_{\ell}(k, r + \varepsilon) - u'_{\ell}(k, r - \varepsilon) = \int_{r-\varepsilon}^{r+\varepsilon} U(r') u_{\ell}(k, r') dr'$$

The total cross section is obtained from Legendre polynomials orthogonality and is: $\sigma_{\text{total}}(k) = \frac{4\pi}{k^2} \sum_{\ell=0}^{\infty} (2\ell+1) \sin^2(\delta_{\ell}(k))$

(Not true for bosons or fermions which need symmetrization) As ℓ increases the centrifugal barrier is more significant and the incident particles need more energy to reach the interaction zone. For a potential of range a , it is enough to take terms up to $\ell_{\text{max}} \simeq ka$. For $ka \ll 1$, $\ell = 0$ (S-wave) dominates.

Low Energy Scattering:

For $k \rightarrow 0$ and $r \gg a$ the radial equation is $u''_{\ell}(k, r) = 0$ with the solution $u_{\ell}(k, r) = C_0(1 - r/\alpha)$, α is called the scattering length. This approximates the real asymptotic form of $u_{\ell}(k, r) \underset{r \rightarrow \infty}{\sim} A_{\ell}(k) \sin[kr - \delta_0(k)]$, and comparing them gives $\alpha = -(\tan \delta_0(k))/k$. Generally if $k \rightarrow 0$ we have $\delta_{\ell}(k) \sim k^{2\ell+1}$, but when there are resonances, i.e. $\alpha \rightarrow \pm\infty$ then $\delta_0(k)$ is finite ($\pm\pi/2$) and $\sigma_{\text{total}} \propto k^{-2} \rightarrow \infty$.

For example, for a potential well of $-V_0$ at $r < b$, this occurs for $\sqrt{2\mu V_0 b^2 / \hbar^2} = (2n+1)\pi/2$.