

Atomic and molecular physics practice course

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1 Classical virial theorem

1.1 Time average for finite motion

Time average:

$$\bar{f} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T f(t) dt \quad (1)$$

Finite motion: the system is stably bound, all coordinates and momenta remain finite.

If the system performs finite motion, then the time average of a full derivative over the time is zero.

$$\overline{\frac{dF}{dt}} \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \frac{dF}{dt} dt = \lim_{T \rightarrow \infty} \frac{F(T) - F(0)}{T} = 0 \quad (2)$$

1.2 Virial theorem

Let us consider a closed, conservative particle system performing finite motion.

$$\overline{\frac{d}{dt} \sum_i \vec{r}_i \vec{p}_i} = 0 \quad (3)$$

$$\frac{d}{dt} \sum_i \vec{r}_i \vec{p}_i = \sum_i \underbrace{\vec{v}_i \vec{p}_i}_{m_i v_i^2 = 2T_i} + \sum_i \vec{r}_i \underbrace{\dot{\vec{p}}_i}_{\vec{F}_i} \quad (4)$$

where we used the formula of kinetic energy T and Newton's law. Time averaging gives

$$2\bar{T} = -\overline{\sum_i \vec{r}_i \vec{F}_i} \quad (5)$$

where $\sum_i \vec{r}_i \vec{F}_i$ is the virial of the system. For closed system, the virial is invariant. Let us move the origin by \vec{r}_0 , then the new coordinates will be $\vec{r}'_i = \vec{r}_i - \vec{r}_0$ and the virial

$$\sum_i \vec{r}'_i \vec{F}_i = \sum_i \vec{r}_i \vec{F}_i - \vec{r}_0 \underbrace{\sum_i \vec{F}_i}_0 = \sum_i \vec{r}_i \vec{F}_i \quad (6)$$

For a conservative system $\vec{F}_i = -\vec{\nabla}_i U = -\frac{\partial U}{\partial \vec{r}_i}$. The final form of the virial theorem

$$2\bar{T} = \overline{\sum_i \vec{r}_i \frac{\partial U}{\partial \vec{r}_i}} \quad (7)$$

1.3 Virial theorem for k-th order homogeneous potential

K-th order homogeneous function:

$$\alpha^k f(x_1, x_2 \dots x_N) = f(\alpha x_1, \alpha x_2 \dots \alpha x_N) \quad (8)$$

where k is a specific constant, $\alpha \in \mathbb{R}$ is arbitrary.

Euler's homogeneous function theorem:

$$\sum_i x_i \frac{\partial f}{\partial x_i} = k f \quad (9)$$

Proof:

Let us differentiate the definition over α , then set $\alpha = 1$.

$$k \alpha^{k-1} f(x_1, x_2 \dots x_N) = \sum_i \frac{\partial f}{\partial \alpha x_i} x_i \quad (10)$$

Virial theorem for k-th order homogeneous potential:

$$2\overline{T} = k\overline{U} \quad (11)$$

Special case: for Coulomb potential $k = -1$ thus $\overline{T} = -\frac{1}{2}\overline{U}$ and $E = \frac{1}{2}\overline{U}$.

2 Virial theorem in quantum mechanics

The time derivative of the expectational value of \hat{A} physical quantity

$$\frac{d}{dt} \langle \Psi | \hat{A} | \Psi \rangle = \left\langle \frac{\partial \Psi}{\partial t} \left| \hat{A} \right| \Psi \right\rangle + \langle \Psi | \frac{\partial \hat{A}}{\partial t} | \Psi \rangle + \left\langle \Psi \left| \hat{A} \right| \frac{\partial \Psi}{\partial t} \right\rangle \quad (12)$$

Using the time dependent Schrödinger equation

$$\frac{\partial \Psi}{\partial t} = -\frac{i}{\hbar} \hat{H} \Psi \quad (13)$$

$$\frac{d}{dt} \langle \Psi | \hat{A} | \Psi \rangle = \left\langle \Psi \left| \frac{\partial \hat{A}}{\partial t} \right| \Psi \right\rangle + \frac{i}{\hbar} \langle \Psi | \hat{H} \hat{A} - \hat{A} \hat{H} | \Psi \rangle \quad (14)$$

For stationary states the expectation value is constant in time. For physical quantities with no explicit time dependence

$$\langle \Psi | [\hat{H}, \hat{A}] | \Psi \rangle = 0 \quad (15)$$

From this follows

$$\left\langle \Psi \left| \left[\hat{H}, \sum_i \hat{r}_i \hat{p}_i \right] \right| \Psi \right\rangle = 0 \quad (16)$$

Using the distributive property of the commutation, we can only concern one particle and one component (let us choose x).

$$\left[\hat{H}, \hat{x} \hat{p}_x \right] = \hat{H} \hat{x} \hat{p}_x - \hat{x} \hat{p}_x \hat{H} + \underbrace{\hat{x} \hat{H} \hat{p}_x - \hat{x} \hat{H} \hat{p}_x}_0 = \hat{x} \left[\hat{H}, \hat{p}_x \right] + \left[\hat{H}, \hat{x} \right] \hat{p}_x \quad (17)$$

Using the form of the Hamiltonian for one particle

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{U} \quad (18)$$

and the canonical commutation relation

$$[\hat{r}_i, \hat{p}_j] = i\hbar \delta_{ij} \quad (19)$$

the commutators to calculate

$$\left[\hat{H}, \hat{x} \right] = \frac{1}{2m} \left[\hat{p}_x^2, \hat{x} \right] = \frac{1}{2m} \left(\hat{p}_x \underbrace{\hat{p}_x \hat{x}}_{\hat{x} \hat{p}_x - i\hbar} - \hat{x} \hat{p}_x \hat{p}_x \right) = \quad (20)$$

$$= \frac{1}{2m} \left(\underbrace{\hat{p}_x \hat{x}}_{\hat{x} \hat{p}_x - i\hbar} \hat{p}_x - i\hbar \hat{p}_x - \hat{x} \hat{p}_x \hat{p}_x \right) = -i\hbar \frac{\hat{p}_x}{m} \quad (21)$$

where we swap $\hat{p}_x \hat{x}$ twice using the canonical commutation relation.

$$\left[\hat{H}, \hat{p}_x \right] = \left[\hat{U}(x), \hat{p}_x \right] = \left[\sum_{n=0}^{\infty} \frac{U^{(n)}}{n!} x^n, \hat{p}_x \right] = \sum_{n=0}^{\infty} \frac{U^{(n)}}{n!} [x^n, \hat{p}_x] \quad (22)$$

where we used the Taylor expansion of the potential.

$$[\hat{x}^n, \hat{p}_x] = i\hbar \hat{x}^{n-1} + \hat{x}^{n-1} \hat{p}_x \hat{x} - \hat{p}_x \hat{x}^n = \dots = i\hbar n \hat{x}^{n-1} \quad (23)$$

where in each step we swap $\hat{x} \hat{p}_x$. The result is

$$\left[\hat{H}, \hat{p}_x \right] = i\hbar \sum_{n=0}^{\infty} \frac{U^{(n)}}{(n-1)!} \hat{x}^{n-1} = i\hbar \frac{\partial U}{\partial x} \quad (24)$$

where we used the Taylor expansion of the derivative function.

Finally the commutation gives

$$\left[\hat{H}, \sum_i \hat{r}_i \hat{p}_i \right] = -i\hbar \left(\underbrace{\sum_i \frac{\hat{p}_i^2}{m_i}}_{2\hat{T}} - \underbrace{\sum_i \hat{r}_i \frac{dU}{d\hat{r}_i}}_{k\hat{U}} \right) \quad (25)$$

and the virial theorem for quantum mechanics reads

$$2 \langle \hat{T} \rangle = k \langle \hat{U} \rangle \quad (26)$$

3 Hydrogen-like atomic orbitals

$$\Psi_{nlm} = R_{nl}(r) Y_l^m(\theta, \phi) \quad (27)$$

where the radial function is

$$R_{nl}(r) = \sqrt{\left(\frac{2Z}{n}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} \left(\frac{2Zr}{n}\right)^l e^{-\frac{Zr}{n}} L_{n-l-1}^{2l+1} \left(\frac{2Zr}{n}\right) \quad (28)$$

with $L_{n-l-1}^{2l+1}(x)$ generalized Laguerre polynomials. The first two of these are

$$L_0^\alpha(x) = 1 \quad (29)$$

$$L_1^\alpha(x) = 1 + \alpha - x \quad (30)$$

The spherical harmonics are

$$Y_l^m(\theta, \phi) = N e^{im\phi} P_l^m(\cos \theta) \quad (31)$$

with $P_l^m(x)$ associated Legendre polynomials. The quantum numbers have the values $n = 1, 2, \dots$; $l = 0, 1, 2, \dots$; $m = -l, \dots, l$. The first few orbitals are

$$1s = \Psi_{100} = 2Z^{\frac{3}{2}} e^{-Zr} \frac{1}{\sqrt{4\pi}} \quad (32)$$

$$2s = \Psi_{200} = \frac{1}{\sqrt{8}} Z^{\frac{3}{2}} (2 - Zr) e^{-\frac{Zr}{2}} \frac{1}{\sqrt{4\pi}} \quad (33)$$

$$2p_0 = \Psi_{210} = \frac{1}{\sqrt{24}} Z^{\frac{3}{2}} Zr e^{-\frac{Zr}{2}} \sqrt{\frac{3}{4\pi}} \cos(\theta) \quad (34)$$

$$2p_{\pm 1} = \Psi_{21\pm 1} = \frac{1}{\sqrt{24}} Z^{\frac{3}{2}} Zr e^{-\frac{Zr}{2}} \sqrt{\frac{3}{8\pi}} \sin(\theta) e^{\pm i\phi} \quad (35)$$

we can see that there are real orbitals, but also complex ones as $2p_{\pm 1}$. But the Schrödinger equation is linear and so the basis functions of a degenerate subspace can be chosen as linear combinations that span the subspace. For example if Ψ_1 and Ψ_2 are eigenstates with energy E , then

$$H(a\Psi_1 + b\Psi_2) = Ea\Psi_1 + Eb\Psi_2 = E(a\Psi_1 + b\Psi_2) \quad (36)$$

the linear combination is also a solution in the same subspace. This can be used to create real atomic orbitals from the linear combinations of degenerate orbitals. $p_{\pm 1}$ orbitals remain degenerate until magnetic interactions are introduced. We can choose the following linear combinations of spherical harmonics that span the m subspace

$$Y_{lm} = \begin{cases} \frac{1}{\sqrt{2}} (Y_l^{-m} + (-1)^m Y_l^m) & m > 0 \\ Y_l^0 & m = 0 \\ \frac{i}{\sqrt{2}} (Y_l^m - (-1)^m Y_l^{-m}) & m < 0 \end{cases} \quad (37)$$

this choice is the same as taking the real and imaginary part or $\cos(\phi)$ and $\sin(\phi)$.

$$p_x = \frac{1}{\sqrt{2}} (p_- + p_+) \quad (38)$$

$$p_y = \frac{i}{\sqrt{2}} (p_- - p_+) \quad (39)$$

This gives the real p-orbital basis of p_x , p_y , p_z . Note that the quantum number m is no longer a good quantum number as the real basis states are no longer L_z eigenstates. The real atomic orbitals can be used as basis functions for calculations or visualization of orbitals.

4 He-like atom perturbational calculation

$$H = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|} \quad (40)$$

where the electron-electron repulsion is considered as perturbation. The unperturbed part is separable in particle indices, thus we can seek the ground state in a product form as $\Psi(1)\Psi(2)$. The Hamilton operator is independent of spin, so the spatial and spin variables can be written in a product form. Since the electron structure of a He-like atom is $(1s)^2$ (aufbau-principle), the unperturbed ground state can be written as the following 1S two-electron singlet (Pauli principle) state:

$$\Psi_0(r_1, s_1, r_2, s_2) = \Phi(100|r_1)\Phi(100|r_2)^1\chi(s_1, s_2) \quad (41)$$

where $\Phi(nlm|r)$ are the hydrogen-like states, $^1\chi(s_1, s_2) = \frac{1}{\sqrt{2}}[\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)]$ is the spin-function. In the expectation value integrals the summation gives 1 as the spin-functions are $\sum_{s_1, s_2} {}^s\chi_m(s_1, s_2) {}^{s'}\chi_{m'}(s_1, s_2) = \delta_{s, s'} \delta_{m, m'}$. The unperturbed ground state energy is two times the hydrogen-like ground state: $E_0^0 = -Z^2$. The first correction to the ground state energy is the Coulomb-integral

$$E_0^1 = J = \left\langle \Psi_0 \left| \frac{1}{r_{1,2}} \right| \Psi_0 \right\rangle \quad (42)$$

After summation to spin variables

$$J = \int d^3r_1 \int d^3r_2 \Phi^*(1) \Phi^*(2) \frac{1}{r_{1,2}} \Phi(1) \Phi(2) = \int d^3r_1 \int d^3r_2 \frac{|\Phi(1)|^2 |\Phi(2)|^2}{r_{1,2}} \quad (43)$$

$$= \int d^3r_1 \int d^3r_2 \frac{\rho(r_1) \rho(r_2)}{r_{1,2}} = \int_{r_1 < r_2} \dots + \int_{r_2 < r_1} \dots = 2 \int_{r_2 < r_1} \dots \quad (44)$$

where we used that the charge densities are the same for the two electrons ($1 \leftrightarrow 2$ index swap). Using the fact that the potential of a spherical charge distribution is the same as the point charge for distances greater than r_{\max} .

$$J = 2 \int d^3r_1 \rho(r_1) \frac{1}{r_1} \int_{r_2 < r_1} d^3r_2 \rho(r_2) \quad (45)$$

$$= 2 \int_0^\infty dr_1 4\pi r_1^2 \rho(r_1) \frac{1}{r_1} \int_0^{r_1} dr_2 4\pi r_2^2 \rho(r_2) \quad (46)$$

Using the radial charge density of s orbital $\rho(r) = \frac{Z^3}{\pi} e^{-2Zr}$.

$$J = 32Z^6 \int_0^\infty dr_1 r_1^2 e^{-2Zr_1} \frac{1}{r_1} \underbrace{\int_0^{r_1} dr_2 r_2^2 e^{-2Zr_2}}_{\left(\frac{\partial}{\partial(-2Z)}\right)^2 \underbrace{\int_0^{r_1} dr e^{-2Zr}}_{\frac{1-e^{-2Zr_1}}{2Z}}} \quad (47)$$

Calculating the derivative

$$\left(\frac{\partial}{\partial 2Z}\right)^2 \frac{1-e^{-2Zr_1}}{2Z} = \left(\frac{\partial}{\partial 2Z}\right) \frac{r_1 e^{-2Zr_1} 2Z - (1-e^{-2Zr_1})}{(2Z)^2} \quad (48)$$

$$= \frac{[(r_1 e^{-2Zr_1} - 2Z r_1^2 e^{-2Zr_1}) - r_1 e^{-2Zr_1}](2Z)^2 - 4Z[r_1 e^{-2Zr_1} 2Z - (1-e^{-2Zr_1})]}{(2Z)^4} \quad (49)$$

and introducing new variable $x = Zr_1$

$$= \frac{4Z}{(2Z)^4} (xe^{-2x} - 2x^2e^{-2x} - 2xe^{-2x} + 1 - e^{-2x}) \quad (50)$$

$$= \frac{1}{4Z^3} \{1 - e^{-2x} (1 + 2x + 2x^2)\} \quad (51)$$

the integration element with the new variable $dr_1 = \frac{dx}{Z}$

$$J = 8Z \int_0^\infty dx xe^{-2x} \{1 - e^{-2x} (1 + 2x + 2x^2)\} = \frac{5}{8}Z \quad (52)$$

5 Hartree-Fock method for helium

What is the best product form wavefunction for He ground state? Let us use the variational principle for a wavefunction $\Psi(1, 2) = \phi(1)\phi(2)$ with the condition $\langle\phi|\phi\rangle = 1$.

$$E_{\text{HF}} = \langle\Psi|H|\Psi\rangle - \lambda \langle\phi|\phi\rangle \quad (53)$$

$$H = h(1) + h(2) + \frac{1}{r_{12}} \quad (54)$$

The variational problem is

$$\delta [\langle\Psi|H|\Psi\rangle - \lambda \langle\phi|\phi\rangle] = 0 \quad (55)$$

$$\langle\Psi|H|\Psi\rangle = 2 \langle\phi|h|\phi\rangle + \left\langle \phi(r_1)\phi(r_2) \left| \frac{1}{r_{12}} \right| \phi(r_1)\phi(r_2) \right\rangle \quad (56)$$

$$\delta \langle\phi|h|\phi\rangle = \langle\delta\phi|h|\phi\rangle + \langle\phi|h|\delta\phi\rangle = \langle\delta\phi|h|\phi\rangle + \langle\delta\phi|h|\phi\rangle^* \quad (57)$$

$$= \langle\delta\phi|h|\phi\rangle + c.c. \quad (58)$$

$$\delta \left\langle \phi(r_1)\phi(r_2) \left| \frac{1}{r_{12}} \right| \phi(r_1)\phi(r_2) \right\rangle = \quad (59)$$

$$= \left\langle \delta\phi(r_1)\phi(r_2) \left| \frac{1}{r_{12}} \right| \phi(r_1)\phi(r_2) \right\rangle + \left\langle \phi(r_1)\delta\phi(r_2) \left| \frac{1}{r_{12}} \right| \phi(r_1)\phi(r_2) \right\rangle + c.c. \quad (60)$$

$$= 2 \left\langle \delta\phi(r_1)\phi(r_2) \left| \frac{1}{r_{12}} \right| \phi(r_1)\phi(r_2) \right\rangle + c.c. \quad (61)$$

where we used the particle exchange symmetry of the potential.

$$\delta [\langle \Psi | H | \Psi \rangle - \lambda \langle \phi | \phi \rangle] = \quad (62)$$

$$2 \int d^3r \delta \phi^*(r) \left(-\frac{1}{2} \Delta - \frac{Z}{r} \right) \phi(r) + 2 \int d^3r \delta \phi^*(r) \left(\int \frac{|\phi(r')|^2}{r_{12}} d^3r' \right) \phi(r) \quad (63)$$

$$- 2E \int d^3r \delta \phi^*(r) \phi(r) + c.c. = 0 \quad (64)$$

Let us calculate the functional derivative with respect to ϕ^* (it can be shown that it is equivalent to variation with ϕ). This way the *c.c.* parts do not give contribution to the variation.

comment: a reminder for the calculation of functional derivative for a general (semilocal) functional

$$F[\rho] = \int f(r, \rho(r), \nabla \rho(r)) d^3r \quad (65)$$

$$\frac{\delta F}{\delta \rho(r)} = \frac{\partial f}{\partial \rho(r)} - \nabla \frac{\partial f}{\partial \nabla \rho(r)} \quad (66)$$

is the Euler-Lagrange equation. For local functional

$$F[\rho] = \int f(r, \rho(r)) d^3r \quad (67)$$

$$\frac{\delta F}{\delta \rho(r)} = \frac{\partial f}{\partial \rho(r)} \quad (68)$$

the functional derivative results in a partial derivative and getting rid of the integration with respect to the variable r of the varied function.

The result of the variation is

$$\frac{\delta [\langle \Psi | H | \Psi \rangle - \lambda \langle \phi | \phi \rangle]}{\delta \phi^*} = \quad (69)$$

$$= \left(-\frac{1}{2} \Delta - \frac{Z}{r} \right) \phi(r) + \left(\int \frac{|\phi(r')|^2}{r_{12}} d^3r' \right) \phi(r) - E \phi(r) = 0 \quad (70)$$

The Hartree-Fock equation is given by

$$(\hat{h} + \hat{J}) \phi(r) = E \phi(r) \quad (71)$$

6 Orthogonalization

Orthogonalization problem arises from the linear variational method, that leads to a generalized matrix eigenvalue problem in the basis of $\{\phi_i\}$

$$\mathbf{H}\mathbf{c} = E\mathbf{S}\mathbf{c} \quad (72)$$

here \mathbf{S} is the matrix of overlap integrals $S_{ij} = \langle \phi_i | \phi_j \rangle$ that is Hermitian by definition and positive definite for linearly independent basis. If the basis is orthonormalized $S_{ij} = \delta_{ij}$ and we can solve a regular eigenvalue problem.

6.1 Gram-Schmidt orthogonalization

The first basis remains unchanged and every other new basis is perpendicular to the new basis set.

$$u_1 = v_1 \quad u_k = v_k - \sum_{j=1}^{k-1} P_{u_j}(v_k) \quad (73)$$

In each step, orthogonalization achieved by subtracting the projection of the current basis element to the already orthogonalized subspace.

$$P_{u_j}(v_k) = \langle u_j | v_k \rangle \frac{u_j}{||u_j||} \quad (74)$$

The problem with this process is that it is non-symmetric.

6.2 Löwdin's orthogonalization

The overlap matrix can be diagonalized by a similarity transformation

$$\mathbf{V}^\dagger \mathbf{S} \mathbf{V} = \mathbf{\Lambda} = \text{diag}(\lambda_i) \quad (75)$$

where \mathbf{V} is unitary ($\mathbf{V}\mathbf{V}^\dagger = 1$) and $\lambda_i > 0$ (positive definite).

Let us define matrix \mathbf{K} by

$$\mathbf{K} = \text{diag} \left(\frac{1}{\sqrt{\lambda_i}} \right) \quad (76)$$

The inverse transformations are

$$\mathbf{V}\mathbf{\Lambda}\mathbf{V}^\dagger = \mathbf{S} \quad (77)$$

$$\mathbf{V}\mathbf{K}\mathbf{V}^\dagger = \mathbf{Z} \quad (78)$$

where $\mathbf{SZ}^2 = 1$ so \mathbf{Z} is the $-\frac{1}{2}$ th power of \mathbf{S} . To prove this

$$\mathbf{SZ}^2 = \mathbf{V}\mathbf{\Lambda}\mathbf{V}^\dagger\mathbf{V}\mathbf{K}\mathbf{V}^\dagger\mathbf{V}\mathbf{K}\mathbf{V}^\dagger = \mathbf{V}\mathbf{\Lambda}\mathbf{K}^2\mathbf{V}^\dagger = 1 \quad (79)$$

So $\mathbf{S}^{-\frac{1}{2}}$ is a Hermitian positive definite matrix with the form

$$\mathbf{S}^{-\frac{1}{2}} = \mathbf{V} \text{diag} \left(\frac{1}{\sqrt{\lambda_i}} \right) \mathbf{V}^\dagger \quad (80)$$

Let us multiply the generalized eigenvalue equation with $\mathbf{S}^{-\frac{1}{2}}$ from the left

$$\underbrace{\mathbf{S}^{-\frac{1}{2}}\mathbf{H}\mathbf{S}^{-\frac{1}{2}}}_{\mathbf{H}'} \underbrace{\mathbf{S}^{\frac{1}{2}}\mathbf{c}}_{\mathbf{d}} = E \underbrace{\mathbf{S}^{-\frac{1}{2}}\mathbf{c}}_{\mathbf{d}} \quad (81)$$

and we get the regular eigenvalue problem.

This transformation of the eigenvalue equation is equivalent with the change of basis to the Löwdin-orthogonalized symmetric basis $\{\psi_i\}$.

$$\psi_i = \sum_{k=1}^m S_{ki}^{-1/2} \phi_k \quad (82)$$

these span the same subspace as $\{\phi_i\}$ but are orthonormalized.

$$\langle \psi_i | \psi_j \rangle = \left\langle \sum_k S_{ki}^{-1/2} \phi_k \left| \sum_l S_{lj}^{-1/2} \phi_l \right. \right\rangle = \sum_{k,l} S_{ik}^{-1/2} \underbrace{\langle \phi_k | \phi_l \rangle}_{S_{kl}} S_{lj}^{-1/2} = \mathbf{S}_{ij}^0 = \delta_{ij} \quad (83)$$

The Hamiltonian matrix element in this Löwdin basis reads

$$\langle \psi_i | \hat{H} | \psi_j \rangle = \left\langle \sum_k S_{ki}^{-1/2} \phi_k \left| \hat{H} \right| \sum_l S_{lj}^{-1/2} \phi_l \right\rangle = \sum_{k,l} S_{ik}^{-1/2} H_{kl} S_{lj}^{-1/2} = H'_{ij} \quad (84)$$

The expansion of a function in the new basis has the form

$$\sum_k c_k \phi_k = \sum_k c_k \sum_l S_{lk}^{1/2} \psi_l = \sum_{k,l} \left(S_{lk}^{1/2} c_k \right) \psi_l = \sum_l d_l \psi_l \quad (85)$$

These are the same as above. Using the orthonormalized Löwdin basis $\{\psi_i\}$, the linear variational problem leads to a standard eigenvalue problem.

6.3 Two dimensional example

Let the basis be ϕ_1, ϕ_2 normalized functions with overlap integral S . The overlap matrix is

$$\mathbf{S} = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix} \quad (86)$$

The eigenvectors and eigenvalues are

$$e_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \lambda_1 = 1 + S \quad (87)$$

$$e_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad \lambda_2 = 1 - S \quad (88)$$

The unitary matrix diagonalizing \mathbf{S} is

$$\mathbf{V} = \begin{pmatrix} e_1^T \\ e_2^T \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \quad (89)$$

and the diagonalized matrix is obviously

$$\mathbf{\Lambda} = \begin{pmatrix} 1 + S & 0 \\ 0 & 1 - S \end{pmatrix} \quad (90)$$

and \mathbf{K} is

$$\mathbf{K} = \begin{pmatrix} \frac{1}{\sqrt{1+S}} & 0 \\ 0 & \frac{1}{\sqrt{1-S}} \end{pmatrix} \quad (91)$$

From this, let us calculate $\mathbf{S}^{-1/2}$

$$\mathbf{S}^{-\frac{1}{2}} = \mathbf{V} \mathbf{K} \mathbf{V}^\dagger = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{1+S}} & 0 \\ 0 & \frac{1}{\sqrt{1-S}} \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} = \quad (92)$$

$$= \frac{1}{2} \begin{pmatrix} \frac{1}{\sqrt{1+S}} + \frac{1}{\sqrt{1-S}} & \frac{1}{\sqrt{1+S}} - \frac{1}{\sqrt{1-S}} \\ \frac{1}{\sqrt{1+S}} - \frac{1}{\sqrt{1-S}} & \frac{1}{\sqrt{1+S}} + \frac{1}{\sqrt{1-S}} \end{pmatrix} \quad (93)$$

The orthonormalized set is

$$\psi_1 = \alpha \phi_1 + \beta \phi_2 \quad (94)$$

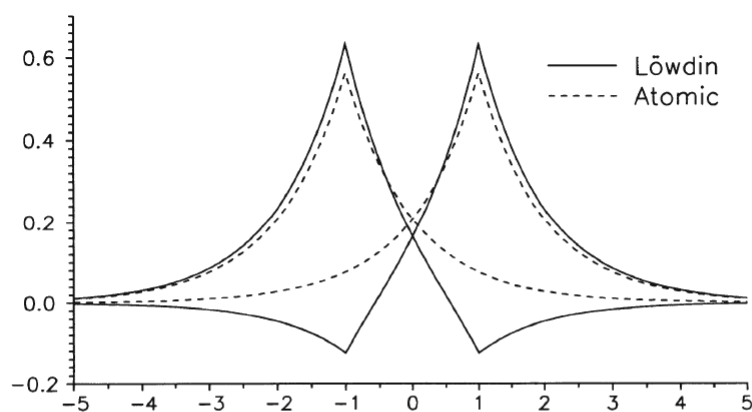
$$\psi_2 = \beta \phi_1 + \alpha \phi_2 \quad (95)$$

where

$$\alpha = \frac{1}{2} \left(\frac{1}{\sqrt{1+S}} + \frac{1}{\sqrt{1-S}} \right) \quad (96)$$

$$\beta = \frac{1}{2} \left(\frac{1}{\sqrt{1+S}} - \frac{1}{\sqrt{1-S}} \right) \quad (97)$$

Figure 1: Figure from Istvan Mayer's book titled Simple Theorems Proofs, and Derivations in Quantum Chemistry



The figure shows the exact atomic $1s$ orbitals of two hydrogen atoms placed at the distance of 2 a.u. (larger than the equilibrium distance of ca. 1.4. a.u. in the H_2 molecule) and their Löwdin-orthogonalized counterparts (S is as large as 0.5865.) It can be seen that the Löwdin orbitals do not differ very much from their overlapping counterparts in the respective “own” atomic region and have a negative cusp on another atom, which provides the resulting orthogonality of the Löwdin orbitals.

7 Linear variation (Ritz method) for excited states of He

$$H = h(1) + h(2) + \frac{1}{r_{12}} \quad (98)$$

$$h = -\frac{1}{2}\Delta - \frac{Z}{r} \quad (99)$$

let ϕ_a and ϕ_b one particle ground and excited eigenstates respectively

$$h(i)\phi_a(r_i) = E_a\phi_a(r_i) \quad h(i)\phi_b(r_i) = E_b\phi_b(r_i) \quad (100)$$

and be ortonormalized

$$\int d^3r \phi_a^*(r)\phi_b(r) = \delta_{ab} \quad (101)$$

The non-interacting two particle basis states are the product of one particle states

$$\psi_1(1, 2) = \phi_a(r_1)\phi_b(r_2) \quad \psi_2(1, 2) = \phi_b(r_1)\phi_a(r_2) \quad (102)$$

The two particle solution approximated by the linear combination

$$\Psi = c_1\psi_1 + c_2\psi_2 \quad (103)$$

Let us solve the generalized eigenvalue problem

$$\mathbf{H}\mathbf{c} = E\mathbf{S}\mathbf{c} \quad (104)$$

The overlap matrix is the identity matrix because

$$S_{11} = \langle \psi_1 | \psi_1 \rangle = \int d^3r_1 \int d^3r_2 \phi_a^*(r_1)\phi_b^*(r_2)\phi_a(r_1)\phi_b(r_2) = \quad (105)$$

$$= \langle \phi_a | \phi_a \rangle \langle \phi_b | \phi_b \rangle = 1 \quad (106)$$

$$S_{22} = \langle \psi_2 | \psi_2 \rangle = 1 \quad (107)$$

$$S_{12} = \langle \psi_1 | \psi_2 \rangle = \int d^3r_1 \int d^3r_2 \phi_a^*(r_1)\phi_b^*(r_2)\phi_b(r_1)\phi_a(r_2) = \quad (108)$$

$$= \langle \phi_a | \phi_b \rangle \langle \phi_b | \phi_a \rangle = 0 \quad (109)$$

$$S_{21} = \langle \psi_2 | \psi_1 \rangle = 0 \quad (110)$$

Let us calculate the Hamiltonian matrix

$$H_{11} = \langle \psi_1 | H | \psi_1 \rangle = \quad (111)$$

$$= \int d^3 r_1 \int d^3 r_2 \phi_a^*(r_1) \phi_b^*(r_2) \left[h(1) + h(2) + \frac{1}{r_{12}} \right] \phi_a(r_1) \phi_b(r_2) \quad (112)$$

$$= E_a + E_b + \underbrace{\int d^3 r_1 \int d^3 r_2 \frac{|\phi_a(r_1)|^2 |\phi_b(r_2)|^2}{r_{12}}}_{J_{ab}} \quad (113)$$

$$H_{22} = \langle \psi_2 | H | \psi_2 \rangle = H_{11} = E_a + E_b + J_{ab} \quad (114)$$

$$H_{12} = \langle \psi_1 | H | \psi_2 \rangle = \quad (115)$$

$$= \int d^3 r_1 \int d^3 r_2 \phi_a^*(r_1) \phi_b^*(r_2) \left[h(1) + h(2) + \frac{1}{r_{12}} \right] \phi_b(r_1) \phi_a(r_2) \quad (116)$$

$$= E_a \underbrace{\langle \phi_a | \phi_b \rangle}_0 \underbrace{\langle \phi_b | \phi_a \rangle}_0 + E_b \underbrace{\langle \phi_a | \phi_b \rangle}_0 \underbrace{\langle \phi_b | \phi_a \rangle}_0 + \quad (117)$$

$$+ \underbrace{\int d^3 r_1 \int d^3 r_2 \phi_a^*(r_1) \phi_b^*(r_2) \frac{1}{r_{12}} \phi_b(r_1) \phi_a(r_2)}_{K_{ab}} \quad (118)$$

$$= K_{ab} \quad (119)$$

$$H_{21} = H_{12} \quad (120)$$

where J is the Coulomb integral and K is the exchange integral. The matrix eigenvalue problem reads

$$\begin{pmatrix} E_a + E_b + J & K \\ K & E_a + E_b + J \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \quad (121)$$

The eigenvectors and eigenvalues are

$$\mathbf{c}_{\text{sym}} = \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad E_+ = E_a + E_b + J + K \quad (122)$$

$$\mathbf{c}_{\text{asym}} = \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad E_- = E_a + E_b + J - K \quad (123)$$

in the sense of the Pauli-principle, the symmetric spatial solution is spin singlet (para He) and the antisymmetric spatial solution is spin triplet (orto He).

8 Fermion wavefunction

8.1 Slater-determinant

Let us construct the wavefunction of N independent fermion. The independence allows us to write the wavefunction in product form of one-particle spin-orbitals, however the wavefunction must be totally antisymmetric in the sense of Pauli-principle. This leads to the Slater-determinant:

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_1(2) & \cdots & \phi_1(N) \\ \phi_2(1) & \phi_2(2) & \cdots & \phi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(1) & \phi_N(2) & \cdots & \phi_N(N) \end{vmatrix} = \frac{1}{\sqrt{N!}} \sum_{i_1, \dots, i_N=1}^N \epsilon_{i_1, \dots, i_N} \phi_{i_1}(1) \cdots \phi_{i_N}(N) \quad (124)$$

where ϵ is the Levi-Civita symbol.

8.2 Separation of orbital and spin part

If the Hamilton operator of the system does not contain spin-operator, then the eigenstates can be separated by orbital and spin functions in a product form

$$\Psi(1, 2, \dots, N) = \Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \chi(s_1, s_2, \dots, s_N) \quad (125)$$

example: two electron wavefunction

$$\Psi(1, 2) = \phi^{\text{sym}}(\mathbf{r}_1, \mathbf{r}_2)^1 \chi(s_1, s_2) \quad (126)$$

$$\Psi(1, 2) = \phi^{\text{asym}}(\mathbf{r}_1, \mathbf{r}_2)^3 \chi(s_1, s_2) \quad (127)$$

for independent electrons in the same orbital

$$\Psi_{aa} = \phi_a(\mathbf{r}_1) \phi_a(\mathbf{r}_2)^1 \chi(s_1, s_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_a(\mathbf{r}_1) \alpha(s_1) & \phi_a(\mathbf{r}_2) \alpha(s_2) \\ \phi_a(\mathbf{r}_1) \beta(s_1) & \phi_a(\mathbf{r}_2) \beta(s_2) \end{vmatrix} \quad (128)$$

for independent electrons in different orbitals

$$\Psi_{ab} = \frac{1}{\sqrt{2}} (\phi_a(\mathbf{r}_1) \phi_b(\mathbf{r}_2) \pm \phi_b(\mathbf{r}_1) \phi_a(\mathbf{r}_2)) \begin{cases} {}^1\chi(s_1, s_2) \\ {}^3\chi(s_1, s_2) \end{cases} \quad (129)$$

homework: Find the Slater-determinant form of

$$\frac{1}{\sqrt{2}} (\phi_a(\mathbf{r}_1) \phi_b(\mathbf{r}_2) + \phi_b(\mathbf{r}_1) \phi_a(\mathbf{r}_2)) \frac{\alpha_1 \beta_2 - \beta_1 \alpha_2}{\sqrt{2}} \quad (130)$$

solution: It cannot be written in one Slater-determinant form

$$\frac{1}{2} \begin{vmatrix} \phi_a(\mathbf{r}_1)\alpha(s_1) & \phi_a(\mathbf{r}_2)\alpha(s_2) \\ \phi_b(\mathbf{r}_1)\beta(s_1) & \phi_b(\mathbf{r}_2)\beta(s_2) \end{vmatrix} - \frac{1}{2} \begin{vmatrix} \phi_a(\mathbf{r}_1)\beta(s_1) & \phi_a(\mathbf{r}_2)\beta(s_2) \\ \phi_b(\mathbf{r}_1)\alpha(s_1) & \phi_b(\mathbf{r}_2)\alpha(s_2) \end{vmatrix} \quad (131)$$

Remember, that this form was the Eckart variational Ansatz, that provided the post Hartree-Fock radial correlation. As the Hartree-Fock solution is the best one Slater-determinant solution, the Eckart-form is a linear combination of Slater-determinants.

9 Hartree-Fock method

Variational method for independent fermion model. Variational Ansatz: one Slater-determinant. The method provides the best approximation for the one particle spin-orbitals. Condition: let the spin-orbitals be orthonormalized:

$$\sum_s \int d^3r \phi_i^*(\mathbf{r}, s) \phi_j(\mathbf{r}, s) = \delta_{i,j} \quad (132)$$

The Hamilton operator

$$H = \sum_i \underbrace{\left[-\frac{1}{2} \Delta_i + V(\mathbf{r}_i) \right]}_{h_i} + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} v(\mathbf{r}_i - \mathbf{r}_j) \quad (133)$$

The energy functional to be minimalized

$$E_{HF} = \langle \Psi | H | \Psi \rangle - \sum_{i,j=1}^N \varepsilon_{j,i} \langle \phi_i | \phi_j \rangle \quad (134)$$

The one-particle operator expectation value is

$$\left\langle \Psi \left| \sum_i h_i \right| \Psi \right\rangle = \sum_{s_1, \dots, s_N} \int d^3r_1 \dots d^3r_N \cdot \quad (135)$$

$$\cdot \sum_{k_1, \dots, k_N} \frac{1}{\sqrt{N!}} \epsilon_{k_1, \dots, k_N} \phi_{k_1}^*(1) \dots \phi_{k_N}^*(N) \cdot \quad (136)$$

$$\cdot \sum_i h_i \sum_{l_1, \dots, l_N} \frac{1}{\sqrt{N!}} \epsilon_{l_1, \dots, l_N} \phi_{l_1}(1) \dots \phi_{l_N}(N) \quad (137)$$

as h_i operates only on the i -th particle, the terms containing $j \neq i$ can be integrated separately

$$= \frac{1}{N!} \sum_{k_1, \dots, k_N} \sum_{l_1, \dots, l_N} \epsilon_{k_1, \dots, k_N} \epsilon_{l_1, \dots, l_N} \sum_{i=1}^N \left[\prod_{j \neq i} \underbrace{\langle \phi_{k_j}(j) | \phi_{l_j}(j) \rangle}_{\delta_{k_j, l_j}} \right] \langle \phi_{k_i}(i) | h_i | \phi_{l_i}(i) \rangle \quad (138)$$

let us do the summation over l_j and swap the indicies of both ϵ until k_i and l_i are the first indicies (this wont change the sign of the expression).

$$= \frac{1}{N!} \sum_{k_i} \sum_{l_i} \underbrace{\sum_{k_1, \dots, k_N} \epsilon_{k_i, k_1, \dots, k_N} \epsilon_{l_i, k_1, \dots, k_N}}_{\delta_{k_i, l_i} (N-1)!} \sum_{i=1}^N \langle \phi_{k_i}(i) | h_i | \phi_{l_i}(i) \rangle \quad (139)$$

$$= \frac{1}{N} \sum_{i=1}^N \sum_{k_i=1}^N \langle \phi_{k_i}(i) | h_i | \phi_{k_i}(i) \rangle = \sum_k \langle \phi_k | h | \phi_k \rangle \quad (140)$$

where we used that the expectation value is independent of the particle index so summation over i gives N .

The expectation value of two-particle operators

$$\left\langle \Psi \left| \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} v(\mathbf{r}_i - \mathbf{r}_j) \right| \Psi \right\rangle = \frac{1}{2} \frac{1}{N!} \sum_{\substack{i,j \\ i \neq j}} \sum_{k_1, \dots, k_N} \sum_{l_1, \dots, l_N} \epsilon_{k_1, \dots, k_N} \epsilon_{l_1, \dots, l_N} \quad (141)$$

$$\cdot \sum_{s_1, \dots, s_N} \int d^3 r_1 \dots d^3 r_N \phi_{k_1}^*(1) \dots \phi_{k_N}^*(N) \frac{1}{r_{i,j}} \phi_{l_1}(1) \dots \phi_{l_N}(N) \quad (142)$$

Doing the same procedure as above, the indicies not equal to i or j can be integrated separately resulting in a Kronecker delta for each kl index pairs. Summation over l indicies gives

$$\frac{1}{2} \frac{1}{N!} \sum_{\substack{i,j \\ i \neq j}} \sum_{k_1, \dots, k_N} \epsilon_{k_1, \dots, k_N} \epsilon_{k_1, \dots, k_N} \sum_{s_i, s_j} \int d^3 r_i d^3 r_j \phi_{k_i}^*(i) \phi_{k_j}^*(j) \frac{1}{r_{i,j}} \phi_{l_i}(i) \phi_{l_j}(j) \quad (143)$$

move the i, j indicies in the Levi-Civita symbols to the front as before (no

sign change).

$$= \frac{1}{2} \frac{1}{N!} \sum_{\substack{i,j \\ i \neq j}} \sum_{k_i, k_j, l_i, l_j} \underbrace{\sum_{k_1, \dots, k_N} \epsilon_{k_i, k_j, k_1, \dots, k_N} \epsilon_{l_i, l_j, k_1, \dots, k_N}}_{(\delta_{k_i, l_i} \delta_{k_j, l_j} - \delta_{k_i, l_j} \delta_{k_j, l_i})(N-2)!} \cdot \quad (144)$$

$$\cdot \sum_{s_i, s_j} \int d^3 r_i d^3 r_j \phi_{k_i}^*(i) \phi_{k_j}^*(j) \frac{1}{r_{i,j}} \phi_{l_i}(i) \phi_{l_j}(j) \quad (145)$$

$$= \frac{1}{2} \frac{1}{N(N-1)} \sum_{\substack{i,j \\ i \neq j}} \left[\sum_{s_i, s_j} \int d^3 r_i d^3 r_j \phi_{k_i}^*(i) \phi_{k_j}^*(j) \frac{1}{r_{i,j}} \phi_{k_i}(i) \phi_{k_j}(j) \right. \quad (146)$$

$$\left. - \sum_{s_i, s_j} \int d^3 r_i d^3 r_j \phi_{k_i}^*(i) \phi_{k_j}^*(j) \frac{1}{r_{i,j}} \phi_{k_j}(i) \phi_{k_i}(j) \right] = \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} (J_{ij} - K_{ij}) \quad (147)$$

Lets do the variation by $\phi_i^*(r, s)$ and recall that it is essentially the same as $\frac{\delta \phi_i^*(r, s)}{\delta \phi_j^*(r', s')} = \delta(r - r') \delta_{s, s'} \delta_{i, j}$, the result is

$$\left(-\frac{1}{2} \Delta + V(r) \right) \phi_i(r, s) + \sum_{\substack{j=1 \\ i \neq j}}^N \sum_{s'} \int d^3 r' \phi_j^*(r', s') v(r - r') \phi_j(r', s') \phi_i(r, s) \quad (148)$$

$$- \sum_{\substack{j=1 \\ i \neq j}}^N \sum_{s'} \int d^3 r' \phi_j^*(r', s') v(r - r') \phi_i(r', s') \phi_j(r, s) = \sum_j \varepsilon_{ji} \phi_j(r, s) \quad (149)$$

Doing the variation with respect to $\phi_i(r, s)$, the left hand side is just complex conjugated

$$c.c. = \sum_j \varepsilon_{ij} \phi_j^*(r, s) \quad (150)$$

substaracting the complex conjugate of latter from the former

$$0 = \sum_j (\varepsilon_{ji} - \varepsilon_{ij}^*) \phi_j^*(r, s) \quad (151)$$

$$\varepsilon_{ji} = \varepsilon_{ij}^* \quad (152)$$

ε is a Hermitian matrix. It can be diagonalized by unitary transformation. In the new basis, the equation remains the same (only ϕ orbitals are changed) and ε is diagonal

$$\left(-\frac{1}{2}\Delta + V(r)\right)\phi_i(r, s) + \sum_{\substack{j=1 \\ i \neq j}}^N \sum_{s'} \int d^3r' \phi_j^*(r', s') v(r - r') \phi_j(r', s') \phi_i(r, s) \quad (153)$$

$$- \sum_{\substack{j=1 \\ i \neq j}}^N \sum_{s'} \int d^3r' \phi_j^*(r', s') v(r - r') \phi_i(r', s') \phi_j(r, s) = \varepsilon_i \phi_i(r, s) \quad (154)$$

We can write these equations in an effective one particle equation

$$\left[-\frac{1}{2}\Delta + V(r) + J_i(r) - K_i\right] \phi_i(r, s) = \varepsilon_i \phi_i(r, s) \quad (155)$$

where the new operators are the Coulomb operator

$$J_i(r) = \sum_{\substack{j=1 \\ i \neq j}}^N \sum_{s'} \int d^3r' \phi_j^*(r', s') v(r - r') \phi_j(r', s') \quad (156)$$

and the exchange operator

$$K_i \phi_i(r, s) = \sum_{\substack{j=1 \\ i \neq j}}^N \phi_j(r, s) \sum_{s'} \int d^3r' \phi_j^*(r', s') v(r - r') \phi_i(r', s') \quad (157)$$

10 Atomic term symbols and Hund's rules

10.1 Atomic structure

orbital approximation: electrons occupy hydrogen-like atomic orbitals leading to electron configuration $1s^2 2s^2 2p^2 \dots$ (note that this is an approximation because the many-particle wavefunction generally can not be constructed as a Slater-determinant). Orbitals of the same n quantum number construct a shell (K, L, M, ... for $n = 1, 2, 3 \dots$) and each shell consists of n subshells of orbitals with the same l quantum number (s, p, d, f, ... for $l = 0, 1, 2, 3 \dots$).

shielding: For hydrogen-like atoms, the energy only depends on quantum number n , but for many-electron atoms the electron-electron interaction removes this degeneracy. This is due to the different nuclear screening constant of different subshells. This leads to difference in shielding (the effective charge of the nucleus felt by the electron in the presence of other electrons) for different subshells. From the radial distribution of orbitals, one can determine the extent of shielding felt by the electron. Close to the core region the shielding increases with increasing l .

Fermi-hole: Another effect that removes degeneracy originates from the Pauli-principle. Parallel spin avoid each other spatially that is called Fermi-hole (spin correlation). This effect decreases the electron-electron repulsion energy thus decreasing the total energy.

10.2 Term symbols

The term symbol notation gives an appropriate labelling of energy levels split by electrostatic interactions described above. The good quantum numbers in the Russell-Saunders (LS) coupling scheme, where the spin-orbit coupling can be treated as a perturbation, are the angular momentum L , spin S and total angular momentum $J = |L - S|, \dots, L + S$ quantum numbers ($\hat{L}\hat{S}$ commutes with \hat{L}^2 , \hat{S}^2 , \hat{J}^2 and \hat{J}_z). The term notation using these

$$^{2S+1}L_J \quad (158)$$

We have seen above that in zeroth order of spin-orbit coupling, the energy levels split by L and S constructing the atomic level structure. In first order of the perturbation, the energy depends on J leading to the **fine structure**.

The construction of term symbols can be made by constructing Slater's table of microstates. Note that a closed shell or subshell indicates $L = 0$ and $S = 0$ from which $J = 0$ leading to a 1S_0 term. Otherwise the only concern is the open subshell. For a subshell l , there are $2(2l + 1)$ possible states for an electron to occupy. If the subshell is filled with N electrons, then the number of microstates is $\binom{2(2l+1)}{N}$. To each microstate, assign the appropriate m_S and m_L quantum numbers. Create a Slater's table with columns of m_S and rows of m_L and fill it with the number of corresponding microstates. From one cell of the table to the other, we can step by using ladder operators for L and S . This means, that we can separate L, S states by finding a maximal m value and stepping down with ladder operators. This way we get ^{2S+1}L , and we can calculate the possible values of $J = |L - S|, \dots, L + S$. Each $^{2S+1}L_J$ term consists of $2J + 1$ microstates.

10.3 Hund's rules

- 1 The term with maximal S lies lowest in energy.
- 2 For given S , the highest L lies lowest in energy.
- 3 For atoms with less than half filled shells, the lowest J lies lower in energy (otherwise the highest J).

example: ground state of nitrogen atom. Electron structure $(1s)^2(2s)^2(2p)^3$, for 2p subshell $l = 1$ and $2(2l + 1) = 6$ so we have 6 slots for the electrons and the number of microstates is 20. (note that the process, in this case, can be shortened by writing down only the microstates with positive m_S and 'mirroring' Slater's table vertically)

$0, \frac{3}{2}$	$-2, \frac{1}{2}$	$-1, \frac{1}{2}$	$0, \frac{1}{2}$	$-1, \frac{1}{2}$																														
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	$-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$
-2				
-1				
0				
1				
2				

After subtracting 4S remains

	$-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$
-2				
-1				
0				
1				
2				

After subtracting 2D remains

	$-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$
-2				
-1				
0				
1				
2				

that is 2P . So the states are ${}^4S_{3/2}$, ${}^2P_{1/2}$, ${}^2P_{3/2}$, ${}^2D_{3/2}$ and ${}^2D_{5/2}$. The highest spin multiplicity is the ground state: ${}^4S_{3/2}$.

11 Dirac equation

Let us consider the relativistic time dependence of a free particle wavefunction. In the sense of the Schrödinger equation, this must be a first order linear partial differential equation in time variable. Relativity theory require the same treatment of spatial variables. In coordiante representation the same relations holds for the relativistic case also:

$$E = i\hbar \frac{\partial}{\partial t} \qquad \hat{\mathbf{p}} = -i\hbar \nabla \qquad (159)$$

So the new Hamilton operator must be linear in $\hat{\mathbf{p}}$

$$\hat{H} = \sum_{i=1}^3 G_i \hat{\mathbf{p}}_i + G_0 m \qquad (160)$$

where G_μ are dimensionless constants, the last part accounts for the rest mass in the total energy. However, the energy-momentum relation must also hold true

$$E^2 = \mathbf{p}^2 + m^2 = \hat{H}^2 \qquad (161)$$

this condition gives us the constraint, that in \hat{H}^2 there are no mixed products. This cannot be done with scalar constants, but rather maticies with the specific anti-commutation relations

$$\{G_\mu, G_\nu\} = 2\delta_{\mu\nu} \qquad (162)$$

with this condition and the generalization for particle in electromagnetic field, the Dirac equation reads

$$i\hbar \frac{\partial \Psi}{\partial t} = \left[\sum_{i=1}^3 G_i (\mathbf{p}_i - q\mathbf{A}_i) + G_0 m + qV \right] \Psi \qquad (163)$$

The anti-commutation relation can be satisfied with 4×4 matrices, but the solution is not unique. The canonical choice is

$$G_0 = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \quad G_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix} \quad (164)$$

where I is the identity matrix and σ_i are the Pauli-matrices.

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (165)$$

notes: the commutation relations of Pauli matrices are

$$\{\sigma_i, \sigma_j\} = 2\delta_{ij} \quad [\sigma_i, \sigma_j] = 2i\epsilon_{ijk}\sigma_k \quad (166)$$

The pauli matrices show the same commutation relation as angular momentum ($\hat{\mathbf{L}}$), this is the intrinsic angular momentum $\hat{\mathbf{S}} = \frac{\hbar}{2}\hat{\sigma}$ called spin.

12 Consequences of Dirac equation

12.1 Conserved quantity

The total time derivative of an operator \hat{A} is

$$i\hbar \frac{d}{dt} \hat{A} = [\hat{A}, \hat{H}] + i\hbar \frac{\partial \hat{A}}{\partial t} \quad (167)$$

If \hat{A} has no explicit time dependence and is a symmetry operator i.e. $[\hat{A}, \hat{H}] = 0$, then it represents a conserved quantity.

- Energy

$$\frac{d}{dt} \hat{H} = \frac{\partial H}{\partial t} \quad (168)$$

for static external fields, the energy of the system is conserved.

non-relativistic cases:

$$H = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m_i} \Delta_i + V_i(\mathbf{r}_i) \right) + \frac{1}{2} \sum_{i \neq j} v_{jk}(\mathbf{r}_j - \mathbf{r}_k) \quad (169)$$

- Momentum

$$\frac{d}{dt} \hat{\mathbf{P}} = - \sum_i \nabla_i V_i(\mathbf{r}_i) \quad (170)$$

for zero external field (closed system), the total momentum of the system is conserved.

- Angular momentum

$$\frac{d}{dt}\hat{\mathbf{L}} = \sum_i \mathbf{r}_i \times (-\nabla_i V_i(\mathbf{r}_i)) \quad (171)$$

in central potential ($\nabla_i V_i(\mathbf{r}_i) \parallel \mathbf{r}_i$), the angular momentum is conserved.

relativistic case:

without magnetic field, in central potential

$$\hat{H} = \sum_{i=1}^3 G_i \mathbf{p}_i + G_0 m + qV \quad (172)$$

$$[\hat{L}_z, G_0 m] = 0 \quad (173)$$

trivially

$$[\hat{L}_z, qV] = 0 \quad (174)$$

in central potential.

$$\left[\hat{L}_z, \sum_{i=1}^3 G_i p_i \right] = \sum_{i=1}^3 G_i [\hat{L}_z, p_i] = \sum_{i=1}^3 G_i [r_1 p_2 - r_2 p_1, p_i] \quad (175)$$

$$[r_1 p_2 - r_2 p_1, p_i] = r_1 \underbrace{[p_2, p_i]}_0 + \underbrace{[r_1, p_i]}_{i\hbar\delta_{1i}} p_2 - r_2 \underbrace{[p_1, p_i]}_0 - \underbrace{[r_2, p_i]}_{i\hbar\delta_{2i}} p_1 = i\hbar (\delta_{1i} - \delta_{2i}) \quad (176)$$

$$\frac{d}{dt}\hat{L}_z = G_1 p_2 - G_2 p_1 \neq 0 \quad (177)$$

so \hat{L} is no more conserved. Let us consider the Pauli matrices (spin operator)

$$[\hat{\sigma}_z, G_0 m] = 0 \quad [\hat{\sigma}_z, qV] = 0 \quad (178)$$

trivially and

$$\left[\hat{\sigma}_z, \sum_{i=1}^3 G_i p_i \right] = \sum_{i=1}^3 [\hat{\sigma}_z, G_i] p_i \quad (179)$$

$$[\hat{\sigma}_z, G_i] = \left[\begin{pmatrix} \sigma_3 & 0 \\ 0 & \sigma_3 \end{pmatrix}, \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix} \right] = \begin{pmatrix} 0 & [\sigma_3, \sigma_i] \\ [\sigma_3, \sigma_i] & 0 \end{pmatrix} \quad (180)$$

$$= \begin{cases} \begin{pmatrix} 0 & 2i\sigma_2 \\ 2i\sigma_2 & 0 \end{pmatrix} = 2iG_2, i = 1 \\ \begin{pmatrix} 0 & -2i\sigma_1 \\ -2i\sigma_1 & 0 \end{pmatrix} = -2iG_1, i = 2 \\ 0, i = 3 \end{cases} \quad (181)$$

$$\frac{d}{dt}\hat{\sigma}_z = -\frac{2}{\hbar}(G_1p_2 - G_2p_1) \quad (182)$$

so the relativistic conserved quantity is the total angular momentum

$$\frac{d}{dt}\left(\hat{L}_z + \frac{\hbar}{2}\hat{\sigma}_z\right) = \frac{d}{dt}\hat{J}_z = 0 \quad (183)$$

This shows that if one uses the correct relativistic formula, it provides the correct treatment of rotations where the spin naturally arises.

12.2 Dirac quasi-particle

Consider the stationary Dirac equation

$$\left[\sum_{i=1}^3 G_i(\mathbf{p}_i - q\mathbf{A}_i) + G_0m + qV \right] \Psi = E\Psi \quad (184)$$

here Ψ has four components, but as we have seen, the G matrix can be separated to 2×2 blocks of Pauli matrices. This decomposition can be made in the wavefunction too

$$\Psi = \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix} = \begin{pmatrix} \Phi \\ \varphi \end{pmatrix} \quad (185)$$

where Φ and φ are the corresponding spinors. We name Ψ a Dirac bispinor. Using the form of G matrices, the stationary equation reads

$$(\mathbf{p} - q\mathbf{A}) \begin{pmatrix} \sigma\varphi \\ \sigma\Phi \end{pmatrix} + m \begin{pmatrix} \Phi \\ -\varphi \end{pmatrix} + qV \begin{pmatrix} \Phi \\ \varphi \end{pmatrix} = E \begin{pmatrix} \Phi \\ \varphi \end{pmatrix} \quad (186)$$

Let us use the total energy formula $E = E' + m$

$$(E' - qV)\Phi - (\mathbf{p} - q\mathbf{A})\sigma\varphi = 0 \quad (187)$$

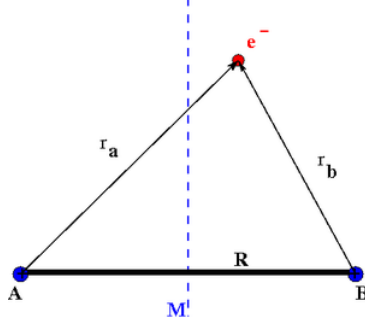


Figure 2: H_2^+ molecule ion parametrization

$$(2m + E' - qV)\varphi - (\mathbf{p} - q\mathbf{A})\sigma\Phi = 0 \quad (188)$$

substituting into each other gives

$$\left[qV + (\mathbf{p} - q\mathbf{A})\sigma \frac{1}{2m + E' - qV} (\mathbf{p} - q\mathbf{A})\sigma \right] \Phi = E'\Phi \quad (189)$$

effective eigenvalue equation. This is similar to the Schrödinger equation of a quasi-particle.

13 H_2^+ molecule ion exact solution

In the Born-Oppenheimer approximation

$$H = -\frac{1}{2}\Delta - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R} \quad (190)$$

The symmetry of the molecule ion makes the prolate spheroidal coordinates the best choice of parametrization.

$$r_a = \frac{R}{2}(\xi + \eta) \quad r_b = \frac{R}{2}(\xi - \eta) \quad (191)$$

$$\xi = \frac{r_a + r_b}{R} \quad \eta = \frac{r_a - r_b}{R} \quad (192)$$

The $\xi = \text{const}$ lines are ellipses with foci A and B nuclei. The $\eta = \text{const}$ lines are hyperbolas with the same foci. The angle of rotation about the molecule axis is φ . ξ plays the role similar to ρ in polar coordinates, while η is similar to $\cos\theta$. The domain of the variables are

$$1 \leq \xi \leq \infty \quad -1 \leq \eta \leq 1 \quad 0 \leq \varphi \leq 2\pi \quad (193)$$

The volume element is

$$dV = \frac{R^3}{8}(\xi^2 - \eta^2) d\xi d\eta d\varphi \quad (194)$$

The Laplacian is

$$\Delta = \frac{4}{R^2(\xi^2 - \eta^2)} \left\{ \frac{\partial}{\partial \xi} \left[(\xi^2 - 1) \frac{\partial}{\partial \xi} \right] + \frac{\partial}{\partial \eta} \left[(1 - \eta^2) \frac{\partial}{\partial \eta} \right] + \left[\frac{1}{\xi^2 - 1} + \frac{1}{1 - \eta^2} \right] \frac{\partial^2}{\partial \varphi^2} \right\} \quad (195)$$

The nuclear attraction terms are

$$-\frac{1}{r_a} - \frac{1}{r_b} = -\frac{4\xi}{R(\xi^2 - \eta^2)} \quad (196)$$

without the nuclear attraction term, the Schrödinger equation is

$$\Delta \Psi + \frac{8\xi}{R(\xi^2 - \eta^2)} \Psi + E\Psi = 0 \quad (197)$$

divided by the prefactor of the laplacian

$$\frac{\partial}{\partial \xi} \left[(\xi^2 - 1) \frac{\partial \Psi}{\partial \xi} \right] + \frac{\partial}{\partial \eta} \left[(1 - \eta^2) \frac{\partial \Psi}{\partial \eta} \right] + \left[\frac{1}{\xi^2 - 1} + \frac{1}{1 - \eta^2} \right] \frac{\partial^2 \Psi}{\partial \varphi^2} \quad (198)$$

$$+ 2R\xi\Psi + \frac{ER^2}{4}(\xi^2 - \eta^2)\Psi = 0 \quad (199)$$

Let the separable Ansatz be

$$\Psi = X(\xi)Y(\eta)F(\varphi) \quad (200)$$

The separation in φ variable

$$\left[\frac{\partial^2}{\partial \varphi^2} + m^2 \right] F(\varphi) = 0 \quad (201)$$

The solution is

$$F(\varphi) = e^{im\varphi} \quad (202)$$

Dividing the Schrödinger equation by Ψ gives the separable form

$$\overbrace{\left\{ \frac{1}{X} [(\xi^2 - 1)X']' - \frac{m^2}{\xi^2 - 1} + 2R\xi + \frac{ER^2}{4}\xi^2 \right\}}^{=\Lambda} + \quad (203)$$

$$\underbrace{\left\{ \frac{1}{Y} [(1 - \eta^2)Y']' - \frac{m^2}{1 - \eta^2} - \frac{ER^2}{4}\eta^2 \right\}}_{=-\Lambda} = 0 \quad (204)$$

where Λ is another separation constant like m . In order to Ψ be a continuous and single-valued function of φ , m must be integer. We have arrived to a form of two coupled ordinary differential eigenvalue problems. The difficulty is the quantization of Λ before we can obtain the energy eigenvalue E . The problem has an exact solution with X and Y in a form of infinite series.

14 H_2^+ molecule ion with LCAO-MO method

Let ϕ_a and ϕ_b be the same normalized atomic orbitals centered on A and B nucleus respectively. The approximation form the molecular orbital is given by the linear combination of these

$$\Psi = c_1\phi_a + c_2\phi_b \quad (205)$$

The generalized Schrödinger equation reads

$$\underline{\underline{H}} \underline{c} = E \underline{\underline{S}} \underline{c} \quad (206)$$

with Hamilton and overlap matrix

$$\underline{\underline{H}} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix} \quad \underline{\underline{S}} = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix} \quad (207)$$

where we used the identity and normalization of the atomic orbitals. The Schrödinger equation ordered to zero is

$$\begin{pmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \quad (208)$$

The secular equation is

$$(\alpha - E)^2 - (\beta - ES)^2 = 0 \quad (209)$$

$$\alpha - E = \pm(\beta - ES) \quad (210)$$

$$E_{\pm} = \frac{\alpha \pm \beta}{1 \pm S} \quad (211)$$

the corresponding eigenfunctions are

$$\Psi_{\pm} = N(\phi_a \pm \phi_b) \quad (212)$$

The normalization factor is

$$\int |\Psi|^2 = N^2 \left(\int |\phi_a|^2 \pm 2 \underbrace{\int \phi_a \phi_b}_S + \int |\phi_b|^2 \right) = 1 \quad (213)$$

$$N = \frac{1}{\sqrt{2(1 \pm S)}} \quad (214)$$

Let us calculate the solution for 1s atomic orbitals.

$$\phi_a(1s|r) = \frac{1}{\sqrt{\pi}} e^{-r_a} \quad (215)$$

For the calculation of S , α and β integrals, we use prolate spheroidal coordinates.

$$S = \int \phi_a(1s|r) \phi_b(1s|r) d^3r = \int \frac{1}{\pi} e^{-(r_a+r_b)} d^3r = \quad (216)$$

$$= \int_0^{2\pi} d\varphi \int_{-1}^1 d\eta \int_1^\infty d\xi \frac{R^3}{8} (\xi^2 - \eta^2) \frac{1}{\pi} e^{-R\xi} = \quad (217)$$

$$= \frac{R^3}{4} \int_{-1}^1 d\eta \int_1^\infty d\xi (\xi^2 - \eta^2) e^{-R\xi} = \frac{R^3}{4} \int_1^\infty d\xi \left[\xi\eta - \frac{1}{3}\eta^3 \right]_{-1}^1 e^{-R\xi} = \quad (218)$$

$$= \frac{R^3}{2} \int_1^\infty d\xi \left(\xi^2 - \frac{1}{3} \right) e^{-R\xi} \quad (219)$$

The last part is

$$-\frac{R^3}{6} \int_1^\infty d\xi e^{-R\xi} = -\frac{R^3}{6} \frac{1}{R} e^{-R} = -\frac{R^2}{6} e^{-R} \quad (220)$$

The first part can be solved by partial integration

$$\frac{R^3}{2} \int_1^\infty d\xi \xi^2 e^{-R\xi} = \frac{R^3}{2} \left(\frac{1}{-R} \underbrace{[\xi^2 e^{-R\xi}]_1^\infty}_{-e^{-R}} - \frac{2}{-R} \underbrace{\int_1^\infty d\xi \xi e^{-R\xi}}_{\frac{1}{-R} [\xi e^{-R\xi}]_1^\infty - \frac{1}{-R} \int_1^\infty d\xi e^{-R\xi}} \right) = \quad (221)$$

$$= \frac{R^2}{2} e^{-R} + R^2 \left(\frac{1}{R} e^{-R} + \frac{1}{R} \frac{1}{R} e^{-R} \right) = \left(\frac{R^2}{2} + R + 1 \right) e^{-R} \quad (222)$$

The two part together gives

$$S = \left(1 + R + \frac{R^2}{3} \right) e^{-R} \quad (223)$$

Let us calculate α now

$$\alpha = \int d^3r \phi_a(1s|r) \hat{H} \phi_a(1s|r) = E_{1s} - j' + \frac{1}{R} \quad (224)$$

where

$$j' = \int d^3r \phi_a(1s|r) \frac{1}{r_b} \phi_a(1s|r) = \int d^3r \frac{1}{\pi} e^{-2r_a} \frac{1}{r_b} = \quad (225)$$

$$= \int_0^{2\pi} d\varphi \int_{-1}^1 d\eta \int_1^\infty d\xi \frac{R^3}{8} (\xi^2 - \eta^2) \frac{1}{\pi} e^{-R(\xi+\eta)} \frac{1}{\frac{R}{2}(\xi - \eta)} = \quad (226)$$

$$= \frac{R^2}{2} \int_{-1}^1 d\eta \int_1^\infty d\xi (\xi + \eta) e^{-R(\xi+\eta)} = \quad (227)$$

$$= \frac{R^2}{2} \underbrace{\int_1^\infty d\xi \xi e^{-R\xi}}_{\left[\left(\frac{\xi}{-R} - \frac{1}{R^2}\right)e^{-R\xi}\right]_1^\infty} \underbrace{\int_{-1}^1 d\eta e^{-R\eta}}_{\frac{1}{-R}(e^{-R} - e^R)} + \frac{R^2}{2} \underbrace{\int_1^\infty d\xi e^{-R\xi}}_{-\frac{1}{-R}e^{-R}} \underbrace{\int_{-1}^1 d\eta \eta e^{-R\eta}}_{\left[\left(\frac{\eta}{-R} - \frac{1}{R^2}\right)e^{-R\eta}\right]_{-1}^1} = \quad (228)$$

$$= \frac{R^2}{2} \left(\frac{1}{-R} - \frac{1}{R^2} \right) e^{-R} \frac{1}{R} (e^{-R} - e^R) + \quad (229)$$

$$+ \frac{R^2}{2} \frac{1}{R} e^{-R} \left[\left(\frac{1}{-R} - \frac{1}{R^2} \right) e^{-R} - \left(\frac{-1}{-R} - \frac{1}{R^2} \right) e^R \right] = \quad (230)$$

$$= 2 \left(-\frac{1}{2} - \frac{1}{2R} \right) e^{-2R} + \frac{1}{2} + \frac{1}{2R} - \frac{1}{2} + \frac{1}{2R} = \frac{1}{R} - \left(1 + \frac{1}{R} \right) e^{-2R} \quad (231)$$

and finally calculate β

$$\beta = \int d^3r \phi_b(1s|r) \hat{H} \phi_a(1s|r) = E_{1s} S - k' + \frac{1}{R} S \quad (232)$$

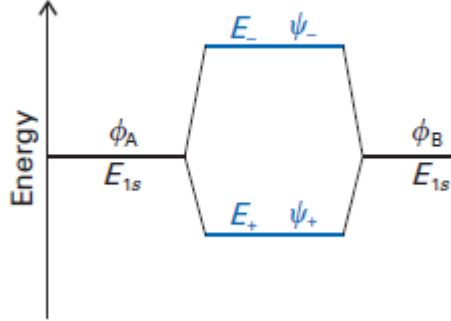
where

$$k' = \int d^3r \phi_b(1s|r) \frac{1}{r_b} \phi_a(1s|r) = \int d^3r \frac{1}{\pi} e^{-(r_a+r_b)} \frac{1}{r_b} = \quad (233)$$

$$= \int_0^{2\pi} d\varphi \int_{-1}^1 d\eta \int_1^\infty d\xi \frac{R^3}{8} (\xi^2 - \eta^2) \frac{1}{\pi} e^{-R\xi} \frac{1}{\frac{R}{2}(\xi - \eta)} = \quad (234)$$

$$= \frac{R^2}{2} \int_1^\infty d\xi e^{-R\xi} \underbrace{\int_{-1}^1 d\eta (\xi + \eta)}_{\left[\xi\eta + \frac{\eta^2}{2}\right]_{-1}^1 = 2\xi} = \frac{R^2}{2} \int_1^\infty d\xi 2\xi e^{-R\xi} = \quad (235)$$

$$= R^2 \frac{1}{-R} \underbrace{\left[\xi e^{-R\xi}\right]_1^\infty}_{-e^{-R}} - \frac{R^2}{-R} \underbrace{\int_1^\infty e^{-R\xi}}_{-\frac{1}{-R}e^{-R}} = (R+1)e^{-R} \quad (236)$$



15 H₂ molecule configurational interaction

Let us recall the solution of H₂⁺ in the 1s orbital basis set.

$$\Psi_{\pm} = \frac{\phi_a \pm \phi_b}{\sqrt{2(1 \pm S)}} \quad (237)$$

these molecule orbitals have $m = 0$ angular momentum quantum number, denoted as σ orbitals. The Ψ_+ orbital has + eigenvalue under inversion noted as gerade σ_g and Ψ_- has - eigenvalue noted as ungerade σ_u . In the MO-LCAO approximation, the molecular orbitals of hydrogen molecule is constructed from the product of H₂⁺ molecular orbitals. This approximation describes an effective independent electron system without electron correlation. The ground and possible excited states in this basis are

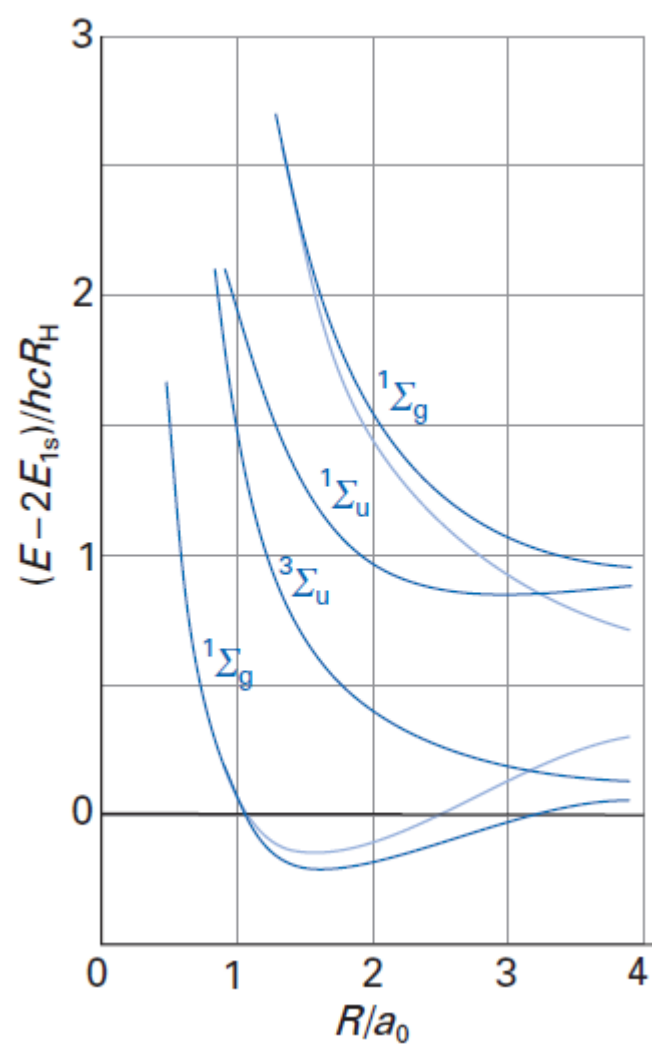
$${}^1\Sigma_g(1, 2) = \sigma_g(1)\sigma_g(2) \quad {}^1\chi(1, 2) \quad (238)$$

$${}^3\Sigma_u(1, 2) = (\sigma_g(1)\sigma_u(2) - \sigma_u(1)\sigma_g(2)) \quad {}^3\chi(1, 2) \quad (239)$$

$${}^1\Sigma_u(1, 2) = (\sigma_g(1)\sigma_u(2) + \sigma_u(1)\sigma_g(2)) \quad {}^1\chi(1, 2) \quad (240)$$

$${}^1\Sigma_g(1, 2) = \sigma_u(1)\sigma_u(2) \quad {}^1\chi(1, 2) \quad (241)$$

This energy ordering is intuitive for shorter R distances, but it is not true for more stretched or broken bond. In the $R \rightarrow \infty$ limit, we expect two separated hydrogen atom. This limit can be achieved with only covalent combinations, this is what VB-theory does by discarding ionic terms. This is not true for MO-theory, because of the equal covalent and ionic contributions, the dissociation energy will lie between the energy of separated hydrogen atoms $H + H$ and separated ions $H^- + H^+$. This originates from the uncorrelated treatment of electrons as they occupy the same molecular orbital leading to no spatial correlation (left-right correlation). This effect is more significant as R increases. The two ${}^1\Sigma_g(1, 2)$ molecular potential energy curves converge



to the same energy as $R \rightarrow \infty$. These two states has the same symmetry therefore never cross. They are split by the interaction (electron-electron repulsion) between them that can be described by configurational interaction (CI). In CI, the ground state is written in a form of linear combination of states with the same symmetry. Here the linear combination reads

$$\phi(1, 2) = c_1 \sigma_g(1) \sigma_g(2) + c_2 \sigma_u(1) \sigma_u(2) \quad (242)$$

Substituting the atomic orbitals into the formula gives

$$\phi(1, 2) = \frac{1}{2}(c_1+c_2) \underbrace{[\phi_a(1)\phi_a(2) + \phi_b(1)\phi_b(2)]}_{\Psi_{\text{ionic}}} + \frac{1}{2}(c_1-c_2) \underbrace{[\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)]}_{\Psi_{\text{covalent}}} \quad (243)$$

with the new mixing coefficients, we introduced a new variable parameter, leading to the lowering of the ground state. The two $^1\Sigma_g(1, 2)$ states are split this way with $R \rightarrow \infty$ limit to $\text{H} + \text{H}$ separated atoms and $\text{H}^- + \text{H}^+$ separated ions.

16 Correlation diagram

Correlation diagram: Energies of molecular orbitals in the function of separation distance $E(R)$. In the $R = 0$ limit, the energies of hydrogen-like orbitals with united nuclei are noted (e.g. $1s\sigma_g$). In the $R \rightarrow \infty$ limit, the atomic orbital energies of separated atoms (e.g. $\sigma_g 1s$). Latter degenerate orbitals are split by the Coulomb interaction, as we have seen it in MO-theory.

$$\sigma_g ns = \phi_{ns}(a) + \phi_{ns}(b) \quad (244)$$

$$\sigma_u^* ns = \phi_{ns}(a) - \phi_{ns}(b) \quad (245)$$

$$\sigma_g np = \phi_{np_z}(a) - \phi_{np_z}(b) \quad (246)$$

$$\pi_u np = \phi_{np_x}(a) + \phi_{np_x}(b) \quad (247)$$

$$\pi_g^* np = \phi_{np_x}(a) - \phi_{np_x}(b) \quad (248)$$

$$\sigma_u^* np = \phi_{np_z}(a) + \phi_{np_z}(b) \quad (249)$$

The ordering of energy can be constructed by considering the constructive and destructive interference of the atomic orbitals. In the case of s orbitals, σ_g molecular orbital lies lower in energy than σ_u^* as the latter has a nodal plane. From the real atomic p orbitals, the overlap of p_z orbitals is the greatest so the energy slitting is also the greatest (with $\sigma_g np$ lying the lowest). Now let us consider the $R \rightarrow 0$ limit. The united atom ns orbital elongates

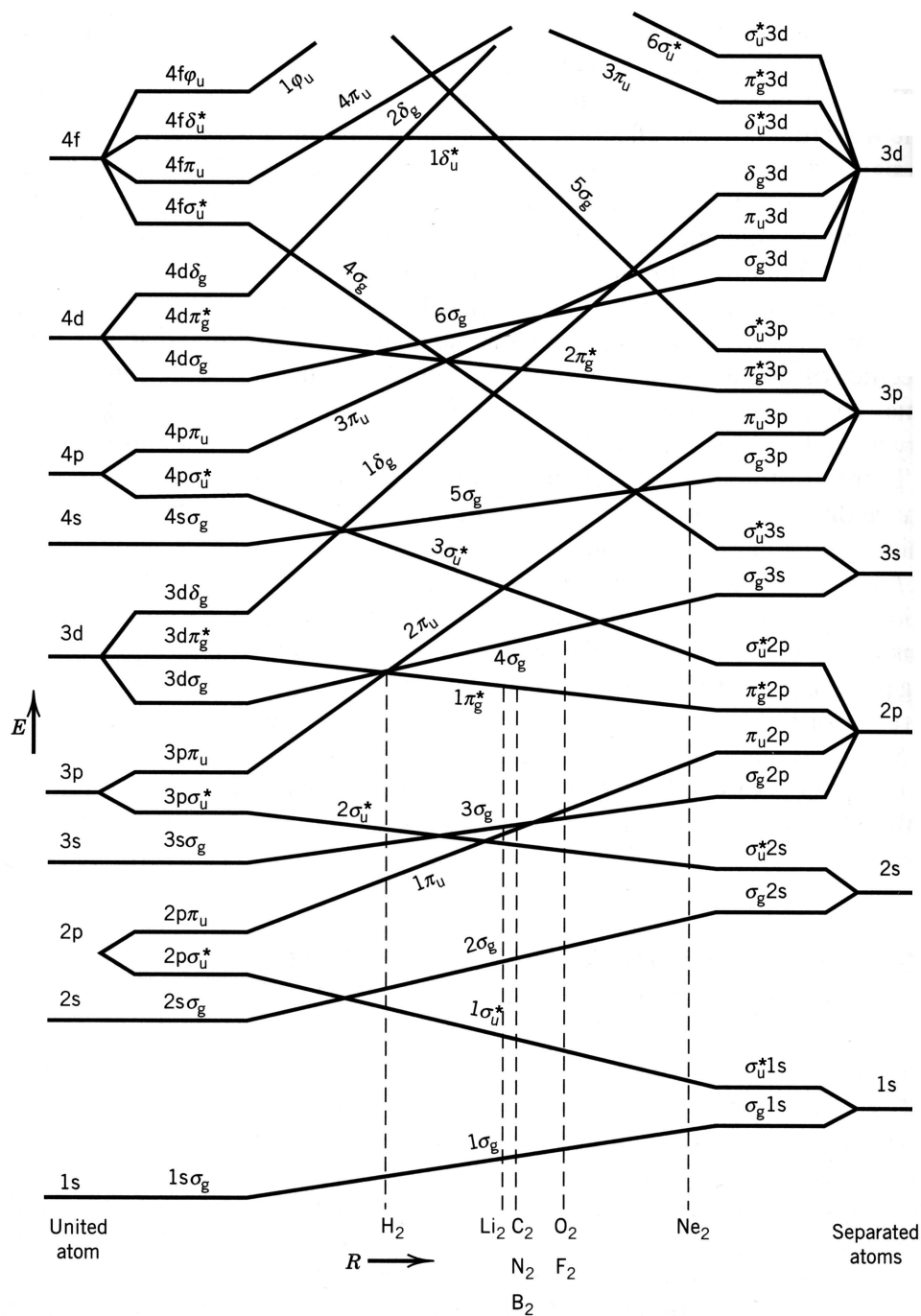


Figure 4: Correlation diagram of homonuclear diatomic molecules

17 Orbital hybridization

We have seen that MO-theory describes molecular orbitals as linear combination of atomic orbitals centered on the nuclei. This leads to good approximation of MO energies and symmetries but in some cases fails to predict the molecular structure (the observed bond angles) and the bonding of some atoms. To correct these, orbital hybridization theory uses hybrid atomic orbitals constructed by the linear combination of different atomic orbitals of the same atom. As the different subshells has different energy, this mixing leads to a promotion in energy thus hybridization is energetically favourable if it leads to stronger bonds (lower molecular orbital energy). Because of this promotion, orbitals of similar energy hybridize.

$$h_a = \sum_i c_{ai} \phi_i \quad (251)$$

where h_a are the hybridized AOs and ϕ_i are the original hydrogen-like AOs. The normalization of the hybrid orbitals reads

$$\sum_i c_{ai}^2 = 1 \quad (252)$$

and require that all AOs are fully utilized in hybridization (except isovalent hybridization)

$$\sum_a c_{ai}^2 = 1 \quad (253)$$

The hybrid orbitals must be orthogonal.

$$\langle h_a | h_b \rangle = \delta_{ab} \quad (254)$$

A very important criteria is that the hybrid orbitals must show the molecule symmetry (they are equivalent against the transformation elements of the symmetry group of the molecule).

17.1 example: hybridization in hydrocarbon molecules

The ground state configuration is $1s^2 2s^2 2p^2$. In the MO teory, carbon atom has a valance of 2, that can form bonds with 90° angle.

However n acetylene C_2H_2 molecule, carbon atom bonds to 2 other atoms in a linear structure with 180° bond angle. This is explained by sp hybridization, $2s$ and $2p_z$ orbitals hybridize and form a σ bond while p_x and p_y form two π bonds. The promotion of an electron is compensated by the greater

overlap of sp hybrid orbitals with the hydrogen s orbitals. Generally the two hybrid orbitals are

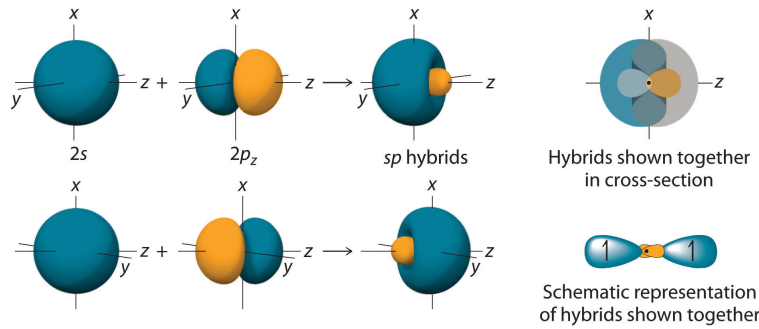
$$h_1 = a_1\phi(2s) + b_1\phi(2p_z) \quad (255)$$

$$h_2 = a_2\phi(2s) + b_2\phi(2p_z) \quad (256)$$

Since the molecule has linear symmetry ($D_{\infty h}$), the hybrid orbitals must contain the same s character: $a_1 = a_2$. Using the completeness and orthonormality equations, the resultant hybrid orbitals are

$$h_1 = \frac{1}{\sqrt{2}} (\phi(2s) + \phi(2p_z)) \quad (257)$$

$$h_2 = \frac{1}{\sqrt{2}} (\phi(2s) - \phi(2p_z)) \quad (258)$$

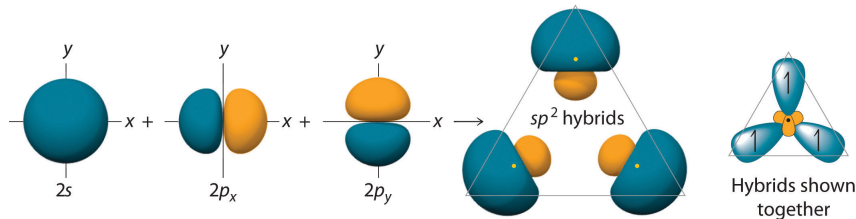


In ethene C_2H_4 molecule, carbon atom bonds to 3 atoms in a trigonal planar structure with 120° bond angle. This is achieved by sp^2 hybridization. Let the molecule plane be xy , thus p_z remains unchanged forming a π bond. The hybrid orbitals forming σ bonds are

$$h_1 = \frac{1}{\sqrt{3}}\phi(2s) + \sqrt{\frac{2}{3}}\phi(p_y) \quad (259)$$

$$h_2 = \frac{1}{\sqrt{3}}\phi(2s) - \frac{1}{\sqrt{6}}\phi(p_y) + \frac{1}{\sqrt{2}}\phi(p_x) \quad (260)$$

$$h_3 = \frac{1}{\sqrt{3}}\phi(2s) - \frac{1}{\sqrt{6}}\phi(p_y) - \frac{1}{\sqrt{2}}\phi(p_x) \quad (261)$$



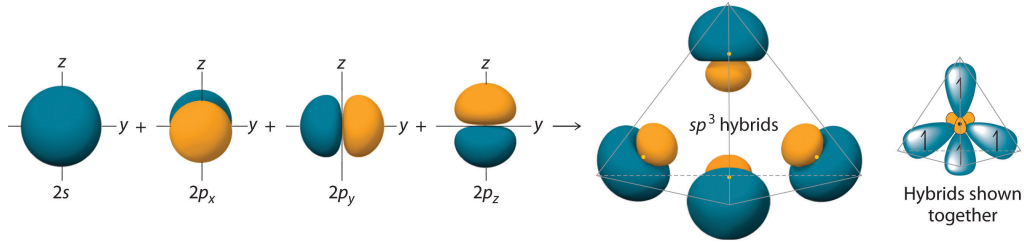
In methane CH_4 molecule, carbon bonds to 4 hydrogen with 109.5° tetrahedral angles. This can be achieved by promotion of an electron from $2s$ to $2p$ subshell and the formation of four sp^3 hybrid orbitals.

$$h_1 = \frac{1}{2} (\phi(2s) + \phi(2p_x) + \phi(2p_y) + \phi(2p_z)) \quad (262)$$

$$h_2 = \frac{1}{2} (\phi(2s) + \phi(2p_x) - \phi(2p_y) - \phi(2p_z)) \quad (263)$$

$$h_3 = \frac{1}{2} (\phi(2s) - \phi(2p_x) + \phi(2p_y) - \phi(2p_z)) \quad (264)$$

$$h_4 = \frac{1}{2} (\phi(2s) - \phi(2p_x) - \phi(2p_y) + \phi(2p_z)) \quad (265)$$



17.2 example: sp hybridization in H_2O molecule

The problem of MO theory predicting bond angle of 90° arises again in water molecule. The experimental bond angle is 104.45° . Let the plane of the molecule be yz , and $2p_x$ is an inert orbital while the hybridization is amongst $2s$, $2p_z$ and $2p_y$. Firstly, we combine the two p orbitals to point along the two bonds with angle θ .

$$p = p_z \cos \frac{\theta}{2} + p_y \sin \frac{\theta}{2} \quad (266)$$

$$p' = p_z \cos \frac{\theta}{2} - p_y \sin \frac{\theta}{2} \quad (267)$$

where we used that the real p orbitals are simply proportional to x , y and z coordinates. The mixing with s orbital must respect the symmetry of the molecule (equal mixing required)

$$h_1 = as + bp \quad h_2 = as + bp' \quad (268)$$

normalization requires

$$a^2 + b^2 = 1 \quad (269)$$

orthogonality requires

$$\langle h_1 | h_2 \rangle = \left\langle as + bp_z \cos \frac{\theta}{2} + bp_y \sin \frac{\theta}{2} \left| as + bp_z \cos \frac{\theta}{2} - bp_y \sin \frac{\theta}{2} \right. \right\rangle = \quad (270)$$

$$= a^2 + b^2 \cos^2 \frac{\theta}{2} - b^2 \sin^2 \frac{\theta}{2} = a^2 + b^2 \cos \theta = 0 \quad (271)$$

where we used the orthonormality of the atomic orbitals. Using the normalization, b can be eliminated

$$a^2 = \frac{\cos \theta}{\cos \theta - 1} \quad (272)$$

this shows us that at 90° bond angle we have pure p orbitals and with increasing bond angle the s character of the hybrid increases until 180° where it reaches 50 – 50 per cent. The third hybrid orbital along z -axis is symmetrically independent from the first two, the general formula is

$$h_3 = a's + b'p_z \quad (273)$$

using orthonormalization

$$a'^2 = \frac{1 + \cos \theta}{1 - \cos \theta} \quad (274)$$

so it changes from pure s to pure p_z as the bond angle increases from 90° to 180° . Notice that for $\theta = 120^\circ$ we get $a^2 = 1/3$, $b^2 = 2/3$, $a'^2 = 1/3$, $b'^2 = 2/3$ that is called sp^2 hybridization.

Now let us see how the electron configuration changes with the bond angle. At the starting 90° angle, we have filled orbitals p_x^2, h_3^2 and bonding orbitals h_1^1, h_2^1 where h_3 is pure s orbital and the bonding orbitals are pure p leading to a configuration s^2p^4 . However at 180° bond angle, h_3 is pure p_z orbital, h_1 and h_2 are 50-50 sp hybrids $s^{1/2}p^{1/2}$ leading to the configuration s^1p^5 . An electron has to be promoted from s to p orbital to achieve this bond angle. With increasing bond angle, the overall promotion is energetically disadvantageous. However the increasing angle lowers the energy by decreasing the electrostatic bond-bond and nuclear repulsion. Furthermore, the increasing s character of the hybrids increases the overlap in the bond formation, lowering the total energy. The competition with the promotion has an optimum at 20% promotion, corresponding to the experimentally measured bond angle.

18 I_h point group

Icosahedral (I_h) point group has the highest group order of 120 amongst the discrete point groups. The C_{60} fullerene has this symmetry. It has

12 pentagon and 20 hexagon faces. The symmetry operations with their corresponding symmetry elements are

Rotations:

- $12C_5$ axis through the pentagon centers by $\pm\frac{2\pi}{5}$
- $20C_3$ axis through the hexagon centers by $\pm\frac{2\pi}{3}$
- $15C_2$ axis through the hexagon-hexagon edge centers by $\frac{2\pi}{2}$

Reflections:

- 15σ plane perpendicular to the opposite hexagon-hexagon edges

Rotoreflections:

- $12S_{10}$ axis through the pentagon centers by $\pm\frac{2\pi}{10}$
- $20S_6$ axis through the hexagon centers by $\pm\frac{2\pi}{6}$

Inversion

Identity

	E	$12C_5$	$12(C_5)^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12(S_{10})^3$	$20S_6$	15σ
A_g	1	1	1	1	1	1	1	1	1	1
T_{1g}	3	$-2\cos(4\pi/5)$	$-2\cos(2\pi/5)$	0	-1	3	$-2\cos(2\pi/5)$	$-2\cos(4\pi/5)$	0	-1
T_{2g}	3	$-2\cos(2\pi/5)$	$-2\cos(4\pi/5)$	0	-1	3	$-2\cos(4\pi/5)$	$-2\cos(2\pi/5)$	0	-1
G_g	4	-1	-1	1	0	4	-1	-1	1	0
H_g	5	0	0	-1	1	5	0	0	-1	1
A_u	1	1	1	1	1	-1	-1	-1	-1	-1
T_{1u}	3	$-2\cos(4\pi/5)$	$-2\cos(2\pi/5)$	0	-1	-3	$2\cos(2\pi/5)$	$2\cos(4\pi/5)$	0	1
T_{2u}	3	$-2\cos(2\pi/5)$	$-2\cos(4\pi/5)$	0	-1	-3	$2\cos(4\pi/5)$	$2\cos(2\pi/5)$	0	1
G_u	4	-1	-1	1	0	-4	1	1	-1	0
H_u	5	0	0	-1	1	-5	0	0	1	-1