Chapter 14
Theorems of Molecular Quantum Mechanics

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ELECTRON PROBABILITY DENSITY

The probability of finding an electron in the rectangular volume element at point \((x, y, z)\) in space with edges \(dx, dy, dz\).

\[
\psi(x_1, \ldots, z_n, m_{s1}, \ldots, m_{sn})^2 \, dx_1 \, dy_1 \, dz_1 \cdots dx_n \, dy_n \, dz_n
\]

spatial and spin coordinates

probability of finding electron 1 with spin \(m_{s1}\) in the volume element \(dx_1, dy_1, dz_1\) at \((x_1, y_1, z_1)\), electron 2 with spin \(m_{s2}\) in the volume element \(dx_2, dy_2, dz_2\) at \((x_2, y_2, z_2)\), and so on.

If not interested in what spin it has, we sum the probability over all possible spin states

\[
\sum_{m_{s1}} \cdots \sum_{m_{sn}} \psi^2 \, dx_1 \cdots dz_n
\]

with no regard for spin
the probability of finding electron 1 in the volume element $dx \, dy \, dz$ at $(x, y, z)$.

\[
\sum_{\text{all } m_i} \cdots \int \left| \psi(x, y, z, x_2, y_2, z_2, \ldots, x_n, y_n, z_n, m_{i1}, \ldots, m_{in}) \right|^2 \times dx_2 \cdots dz_n \, dx \, dy \, dz
\]

a $(3n - 3)$-fold integration over $x_2$ through $z_n$.

the probability of finding electron 2 in the volume element $dx \, dy \, dz$ at $(x, y, z)$.

\[
\sum_{\text{all } m_i} \cdots \int \left| \psi(x_1, y_1, z_1, x, y, z, x_3, \ldots, z_n, m_{i1}, \ldots, m_{in}) \right|^2 \times dx_1 \, dy_1 \, dz_1 \, dx_3 \cdots dz_n \, dx \, dy \, dz
\]

Indistinguishability of electrons: $\psi_1 = \psi_2$

$\psi$ is antisymmetric with respect to electron exchange, and therefore $\psi^2$ is unchanged.

\[1\] the probability of finding any one particular electron in the volume element.

the probability of finding an electron in the volume element is $(n \times 1)$.

the probability density $p$ for finding an electron in the neighborhood of point $(x, y, z)$ is:

\[
p(x, y, z) = n \sum_{\text{all } m_i} \cdots \int \left| \psi(x, y, z, x_2, \ldots, z_n, m_{i1}, \ldots, m_{in}) \right|^2 \, dx_2 \cdots dz_n
\]

$\rho(r) = n \sum_{\text{all } m_i} \cdots \int \left| \psi(r, r_2, \ldots, r_n, m_{i1}, \ldots, m_{in}) \right|^2 \, dr_2 \cdots dr_n$

vector notation for spatial variables

atomic units: electrons/bohr$^3$
Experimental determination of $\rho$ of a molecule:
1) x-ray diffraction intensities of molecular crystals
2) electron-diffraction intensities of gases.

the electron density for the simple VB and MO gs $H_2$ functions

$$\rho(r) = n \sum \int \int \cdots \int \left| \psi(r, r_2, \ldots, r_m, m_{x1}, \ldots, m_{xn}) \right|^2 \, dr_2 \cdots dr_n$$

Summation over $m_{x1}$ and $m_{x2}$ gives unity

$$\rho(x, y, z) = 2 \int \int \int \phi(x, y, z, x_2, y_2, z_2) \, dx_2 \, dy_2 \, dz_2$$

spatial factor

Exercise: Derive eqs for $\rho_{\text{VB}}$ and $\rho_{\text{MO}}$.

$\phi_{\text{MO}} = \frac{1}{2(1 + S_{ab})} [1s_a(1) + 1s_b(1)][1s_a(2) + 1s_b(2)]$

$$\phi_{\text{VB}} = \frac{1s_a(1)1s_b(2) + 1s_a(2)1s_b(1)}{\sqrt{2(1 + S_{ab})^{1/2}}}$$

$$\rho_{\text{VB}} = \frac{1s_a^2 + 1s_b^2 + 2S_{ab}1s_a1s_b}{1 + S_{ab}}, \quad \rho_{\text{MO}} = \frac{1s_a^2 + 1s_b^2 + 2 \cdot 1s_a1s_b}{1 + S_{ab}}$$

Exercise: Derive eqs for $\rho_{\text{VB}}$ and $\rho_{\text{MO}}$.

$\checkmark \rho_{\text{MO}} \geq \rho_{\text{VB}}$ at the midpoint of the bond $\rightarrow$ piles up more charge between the nuclei than the VB function (MO function underestimates electron correlation)
For $H_2^+$-like MO: \[ \phi_i^2 = \frac{1}{2(1 + S_{ab})} [1s_a^2 + 1s_b^2 + 2(1s_a 1s_b)] \]

\( \rho_{\text{MO}} = 2 \times \rho \) (for $H_2^+$-like MO)

can prove, for a many-electron MO wave function:
\[ \rho = \sum \rho_{\text{each MO}} \times n_e \text{(occupying it)} \]

\[ \rho(x, y, z) = \sum_j n_j |\phi_j|^2 \]

over different orthogonal spatial MOs

the number of electrons in the MO \( \phi_j \) (0, 1, or 2)

from SCF wave functions: maxima in \( \rho \) occur only at the nuclei

Exceptions: gs of Li\(_2\) and Na\(_2\) (a small local maximum at the bond midpoint)

\( B(\mathbf{r}_i) \): a function of the spatial coordinates \( x_i, y_i, z_i \) of electron \( i \)

the average value

\[ \left\langle \psi \left| \sum_{i=1}^{n} B(\mathbf{r}_i) \right| \psi \right\rangle = \int \psi^* \sum_{i=1}^{n} B(\mathbf{r}_i) \psi \ d\tau = \sum_{i=1}^{n} |\psi|^2 B(\mathbf{r}_i) \ d\tau \]

electronic wave function.

electrons are indistinguishable: terms are identical

\[ \left\langle \psi \left| \sum_{i=1}^{n} B(\mathbf{r}_i) \right| \psi \right\rangle = \int n |\psi|^2 B(\mathbf{r}_i) \ d\tau \]
The dipole moment function $B(r)$ depends only on $x_1, y_1, z_1$ before we integrate over $x_1, y_1, z_1$, we can integrate $n |\psi|^2$ over the spatial coordinates of electrons 2 to $n$ and sum over all the spin coordinates.

$$\rho(r) = n \sum_{i=1}^{n} \cdots \int |\psi(r, x_2, \ldots, x_n, m_2, \ldots, m_n)|^2 \, dx_2 \cdots dx_n$$

$$\langle \psi | \sum_{i=1}^{n} B(r_i) | \psi \rangle = \int \rho(r) B(r) \, dr$$

over the three spatial coordinates $x, y, z$.

**DIPOLE MOMENTS**

Wave functions $\rightarrow$ molecular dipole moments

**Classical expression:**

For a set of discrete charges $Q_i$,

$$\mu_{ci} = \sum_{i} Q_i x_i$$

Position vector

Its $x$ component:

$$\mu_{x,ci} = \sum_{i} Q_i x_i$$
For a continuous charge distribution with charge density $\rho_Q(x, y, z)$

$$dQ = \rho_Q(x, y, z) \, dx \, dy \, dz$$

$$\mu_{cl} = \int dQ$$

$$\mu_d = \int \rho_Q(x, y, z) r \, dx \, dy \, dz,$$

where $r = xi + yj + zk$

quantum-mechanical definition of the electric dipole moment:

a uniform external electric field $E \rightarrow$ the effect on the energy of atom or molecule

classical expression for $E \rightarrow$ form the Hamiltonian operator

\[ \frac{dV}{dz} = -F_z \]

\[ E = F/Q \]

\[ E = F/Q \]

\[ \frac{dV}{dz} = -Q\varepsilon_z \]

\[ V = -Q\varepsilon_z z \]

the potential energy of a single charge in the field.

\[ V = -\varepsilon_z \sum_i Q_i z_i \]

a system of charges

where the electric field points in an arbitrary direction:

\[ V = -\varepsilon_z \sum_i Q_i x_i - \varepsilon_y \sum_i Q_i y_i - \varepsilon_z \sum_i Q_i z_i = -E \cdot \mu_d \]

energy of an electric dipole in a uniform applied electric field (classical-mechanical expression).
quantum-mechanical expression (by perturbation theory):

\[ \hat{H}' = -E \cdot \hat{\mu} \]

\[ \hat{\mu} = \sum_i Q_i \hat{x}_i = i \hat{\mu}_x + j \hat{\mu}_y + k \hat{\mu}_z \]

electric dipole-moment operator

\[ \hat{\mu}_x = \sum_i Q_i x_i, \quad \hat{\mu}_y = \sum_i Q_i y_i, \quad \hat{\mu}_z = \sum_i Q_i z_i \]

The first-order correction:

\[ E^{(1)} = -E \cdot \int \psi^{(0)*} \hat{\mu} \psi^{(0)} \, d\tau \]

unperturbed wave function.

\[ \mu = \int \psi^{(0)*} \hat{\mu} \psi^{(0)} \, d\tau \]

quantum-mechanical electric dipole moment

Only the first-order energy correction considered

permanent electric dipole moment.

field distorts the wave function from \( \psi^{(0)} \)

induced electric dipole moment (corresponds to the energy correction \( E^{(2)} \))

\[ \mu_{\text{ind}} = \alpha E \]

\( \alpha \) = polarizability of the atom or molecule.

Higher \( \alpha \) → higher London dispersion force (between two B molecules).

Stark effect: The shift in the energy of a quantum-mechanical system by an applied electric field.

The first-order (or linear) Stark effect: is given by \( E^{(1)} = -E \cdot \int \psi^{(0)*} \hat{\mu} \psi^{(0)} \, d\tau \)

FOSE is vanishes \( \leftarrow \) permanent electric dipole moment = 0

The second-order (or quadratic) Stark effect: is given by \( E^{(2)} \) and is proportional to the square of the applied field.

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in electronic state $\psi_{el}$:

$$\mu = \int \psi_{el}^* \hat{\mu} \psi_{el} \, d\tau_{el}$$

permanent electric dipole moment

For homonuclear diatomic molecules $\psi_{el}$ is g or u $\rightarrow \mu = 0$

For any molecule with a center of symmetry $\mu = 0$.

for a molecule:

$$\hat{\mu} = \sum_i (-e\mathbf{r}_i) + \sum_{\alpha} Z_{\alpha} e\mathbf{r}_{\alpha}$$

$r_{\alpha}$ is the vector from the origin to the nucleus $\alpha$

$r_i$ is the vector to electron $i$.

Since $\hat{\mu}$ and the $\psi_{el}$ depend on the parameters defining the nuclear configuration, $\mu$ depends on the nuclear configuration.

(a) $\mu = \int \psi_{el}^* \hat{\mu} \psi_{el} \, d\tau_{el}$ ignored the nuclear motion dipole-moment function

experimentally determined: what is measured is (a) averaged over the zero-point vibrations (assuming the temperature is not high enough for there to be appreciable population of higher vibrational levels).

$\mu_0$: dipole moment averaged over zero-point vibrations

$\mu_e$: dipole moment at the equilibrium nuclear configuration

$$\mu = \int \psi_{el}^* \hat{\mu} \psi_{el} \, d\tau_{el}$$

$$\hat{\mu} = \sum_i (-e\mathbf{r}_i) + \sum_{\alpha} Z_{\alpha} e\mathbf{r}_{\alpha}$$

$$\mu = \int \psi_{el}^* \sum_i (-e\mathbf{r}_i) \psi_{el} \, d\tau_{el} + \sum_{\alpha} Z_{\alpha} e\mathbf{r}_{\alpha}$$

$$\mu = \int \int \rho(x, y, z) \mathbf{r} \, dx \, dy \, dz + e \sum_{\alpha} Z_{\alpha} \mathbf{r}_{\alpha}$$

$$\mu = -e \int \int \rho(x, y, z) \mathbf{r} \, dx \, dy \, dz + e \sum_{\alpha} Z_{\alpha} \mathbf{r}_{\alpha}$$

electron probability density.
THE HARTREE-FOCK METHOD FOR MOLECULES

A key development in quantum chemistry has been the computation of accurate self-consistent-field wave functions for many diatomic and polyatomic molecules.

For closed shells:
The molecular HF wave function is an antisymmetrized product (Slater determinant) of spin-orbitals.

By the variation theorem: $E_{HF} = \langle D | \hat{H}_{el} + V_{NN} | D \rangle$

$D$: Slater-determinant HF wave function (normalized)
$V_{NN}$: does not involve electronic coordinates

\[
\hat{H}_{el} = \sum_i \hat{f}_i + \sum_{i>j} \hat{g}_{ij}
\]

one-electron operators
\[
\hat{f}_i = -\frac{1}{2} \nabla_i^2 - \sum_a Z_a/r_{ia}
\]

two-electron operators
\[
\hat{g}_{ij} = 1/r_{ij}
\]

\[
\langle D | \hat{H} | D \rangle = \sum_{i=1}^{n} \langle \phi_i(1) | \hat{f}_i | \phi_i(1) \rangle + \sum_{i,j=1}^{n} \sum_{\mu, \nu} (J_{ij} - \delta_{\mu, \nu} K_{ij})
\]

\[
J_{ij} = \langle \phi_i(1) \phi_j(2) | e^2/r_{ij} | \phi_i(1) \phi_j(2) \rangle
\]

\[
K_{ij} = \langle \phi_i(1) \phi_j(2) | e^2/r_{ij} \phi_i(1) \phi_j(2) \rangle
\]

\[
\hat{f}_i = -(\hbar^2/2m_e) \nabla_i^2 - Ze^2/r_i
\]

\[
E = \langle D | \hat{H} | D \rangle = 2 \sum_{i=1}^{n} \frac{\hbar^2}{2m_e} \langle \phi_i(1) | \hat{f}_i | \phi_i(1) \rangle + \sum_{i,j=1}^{n} \sum_{\mu, \nu} (2J_{ij} - K_{ij})
\]
The Hartree-Fock method looks for those orbitals \( \phi_i \) that minimize the variational integral \( E_{\text{HF}} \).

MO is taken to be normalized: \( \langle \phi_i(1)|\phi_i(1) \rangle = 1 \)

for computational convenience one takes the MOs to be orthogonal:

\( \langle \phi_i(1)|\phi_j(1) \rangle = 0 \) for \( i \neq j \)

a lower energy is not obtained in the absence of the orthogonality restriction

Pauli antisymmetry requirement removes nonorthogonalities from the orbitals.
the closed-shell orthogonal Hartree-Fock MOs satisfy:

\[ \hat{F}(1)\phi_i(1) = \epsilon_i \phi_i(1) \]

\( \epsilon_i \): the orbital energy

\[ \hat{F}(1) = \hat{H}_{\text{core}}(1) + \sum_{j=1}^{n^2} [2\hat{j}(1) - \hat{K}_j(1)] \]

\( \hat{H}_{\text{core}}(1) = -\frac{1}{2} \nabla_i^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{1\alpha}} \)

\( \hat{j}(1) = \) kinetic energy operator of one electron

\( \hat{K}_j(1) = \) potential-energy operators for the attractions between one electron and the nuclei

\( \phi_i(1) \): an arbitrary function

\( f(1) \): the potential energy of interaction between electron 1 and a smeared-out electron with electronic density \( |\phi_j(2)|^2 \)

\( \frac{1}{r_{12}} \): Coulomb operator

\( \phi_j^*(2)f(2) \): exchange operator

\( \frac{1}{r_{12}} \): has no simple physical interpretation

\( \frac{1}{r_{12}} \): arises from the requirement that the wave function be antisymmetric with respect to electron exchange.

\( n \): there are two electrons in each spatial orbital

\( \hat{K}_j(1) = \phi_j(1) \int \frac{\phi_j^*(2)f(2)}{r_{12}} \, dv_2 \)

\( \frac{1}{r_{12}} \): over all space

\( \frac{1}{r_{12}} \): The orthogonality of the MOs greatly simplifies calculations (simpler)

\( \frac{1}{r_{12}} \): The VB method uses atomic orbitals, and AOs centered on different atoms are not orthogonal.
The true Hamiltonian operator and wave function involve the coordinates of all n electrons.

The Hartree-Fock Hamiltonian operator $\hat{F}$ is a one-electron operator

The operator $\hat{F}$ depends on its own eigenfunctions, which are not known initially. Hence the Hartree-Fock equations must be solved by an iterative process.

\[
\hat{F}(1)\phi_i(1) = e_i\phi_i(1)
\]

a one-electron differential equation

\[
e_i = \int \phi_i^*(1)\hat{F}(1)\phi_i(1) \, dv_i
\]

multiply by $\phi_i^*(1)$
integrate over all space

\[
\hat{F}(1) = \hat{H}_{\text{core}}(1) + \sum_{i=1}^{n/2} [2\hat{J}_{ij}(1) - \hat{K}_{ij}(1)]
\]

\[
e_i = \langle \phi_i(1) | \hat{H}_{\text{core}}(1) | \phi_i(1) \rangle + \sum_j [2\langle \phi_i(1) | \hat{J}_{ij}(1) | \phi_i(1) \rangle - \langle \phi_i(1) | \hat{K}_{ij}(1) | \phi_i(1) \rangle]
\]

\[
e_i = H_{ii}^{\text{core}} + \sum_{j=1}^{n/2} (2J_{ij} - K_{ij})
\]
Roothaan's proposal: expand the spatial orbitals $\phi_i$ as linear combinations of a set of one-electron basis functions $\chi_s$ (make feasible the calculation)

$$\phi_i = \sum_{s=1}^{b} c_{is} \chi_s$$

basis functions should form a complete set (exact representation, infinite number of basis functions)

In practice: a finite number $b$ of basis functions

negligible error in MOs representation: $b$ be large enough and the functions $\chi_s$ well chosen

\[
\hat{F}(1)\phi_i(1) = \varepsilon_i \phi_i(1)
\]

\[
\phi_i = \sum_{s=1}^{b} c_{is} \chi_s
\]

\[
\sum_{s} c_{is} \hat{F} \chi_s = \varepsilon_i \sum_{s} c_{is} \chi_s
\]

$x_i^r \times$ and integration

\[
\sum_{s=1}^{b} c_{ir} (F_{rs} - \varepsilon_n S_{rs}) = 0, \quad r = 1, 2, \ldots, b
\]

\[
F_{rs} = \langle \chi_r | \hat{F} | \chi_s \rangle \quad S_{rs} = \langle \chi_r | \chi_s \rangle
\]
For a nontrivial solution:

$$\sum_{s=1}^{b} c_{si}(F_{rs} - \epsilon_r S_{rs}) = 0, \quad r = 1, 2, \ldots, b$$  

a secular equation

Roothaan equations must be solved by an iterative process, since the \( F_{rs} \)
depend on the orbitals \( \phi_i \) (through the dependence of \( \tilde{F} \) on the \( \phi_i \)'s),
which depend on \( c_{si} \).
Basis functions:

✓ Generally, each MO is written as a linear combination of one-electron functions (orbitals) centered on each atom.

✓ one can use Slater functions for the AOs.

✓ a complete set of AO BFs: an infinite number of SOs are needed,

✓ the true molecular HF wave function can be closely approximated with a reasonably small number of carefully chosen SOs.

✓ A minimal BS for a molecular SCF calculation consists of a single basis function for each inner-shell AO and each valence-shell AO of each atom.

✓ An extended basis set (EBS) is a set that is larger than a minimal set.

✓ Minimal-BS SCF calculations are easier than EBS calculations, but the latter are considerably more accurate.
SCF wave function and Hartree-Fock wave function

the term SCF wave function is applied to any wave function obtained by iterative solution of the Roothaan equations

the basis set is large enough to give a really accurate approximation to the HF SCF wave function.

There is only one true HF SCF wave function, which is the best possible wave function that can be written as a Slater determinant of spin-orbitals.

By the extended-basis-set calculations \( \rightarrow \) "near HF wave functions" or, less cautiously, "HF wave functions."

The Fock Matrix Elements

To solve the Roothaan equations:
1) express the Fock matrix elements (integrals) \( F_{rs} \) in terms of \( \chi \)

\[
F_{rs} = \langle \chi_r(1)|\hat{F}(1)|\chi_s(1)\rangle = \langle \chi_r(1)|\hat{H}_{\text{core}}(1)|\chi_s(1)\rangle + \sum_{j=1}^{n/2} [2\langle \chi_r(1)|\hat{j}(1)|\chi_s(1)\rangle - \langle \chi_r(1)|\hat{\kappa}(1)|\chi_s(1)\rangle]
\]

the basis functions \( = \chi \)
Fock operator = \( \hat{F} \)

\[
\hat{F}(1) = \hat{H}_{\text{core}}(1) + \sum_{j=1}^{n/2} [2\hat{j}(1) - \hat{\kappa}(1)]
\]
\[ \hat{J}_1(1)f(1) = f(1) \int \left| \phi_i(2) \right|^2 \frac{1}{r_{12}} \, dv_2 \]
\[ \phi_i = \sum_{s=1}^{b} c_s \chi_s \quad i \rightarrow \chi \]
\[ \hat{J}_1(1)\chi_s(1) = \chi_s(1) \int \frac{\phi_i^*(2)\phi_i(2)}{r_{12}} \, dv_2 = \chi_s(1) \sum_{a} c_{a1}^c c_{a2}^d \int \frac{\chi_i^*(2)\chi_a(2)}{r_{12}} \, dv_2 \]
\[ \chi_s^*(l) \times \]
integration over the coordinates of electron 1

\[ \langle \chi_s(1) | \hat{J}_1(1) | \chi_s(1) \rangle = \sum_{a} c_{a1}^c c_{a2}^d \int \frac{\chi_i^*(2)\chi_s(1)\chi_i^*(2)\chi_a(2)}{r_{12}} \, dv_1 \, dv_2 \]

\[ \langle \chi_s(1) | \hat{J}_1(1) | \chi_s(1) \rangle = \sum_{l=1}^{b} \sum_{u=1}^{b} c_{l}^c c_{u}^d \langle rs|lu \rangle \quad \text{two-electron repulsion integral} \]

\[ \hat{K}_1(1)f(1) = f(1) \int \frac{\phi_i^*(2)f(2)}{r_{12}} \, dv_2 \]
\[ \phi_i = \sum_{s=1}^{b} c_s \chi_s \quad f \rightarrow \chi \]
\[ \chi_s^*(l) \times \]
integration over the coordinates of electron 1

\[ \langle \chi_s(1) | \hat{K}_1(1) | \chi_s(1) \rangle = \sum_{l=1}^{b} \sum_{u=1}^{b} c_{l}^c c_{u}^d \langle rs|lu \rangle \]
\begin{align*}
F_{rs} &= \langle \chi_r(1)|\hat{H}(1)|\chi_s(1) \rangle = \langle \chi_r(1)|\hat{H}^{\text{core}}(1)|\chi_s(1) \rangle \\
&\quad + \sum_{f=1}^{n/2} [2\langle \chi_r(1)|\hat{J}(1)|\chi_s(1) \rangle - \langle \chi_r(1)|\hat{K}(1)|\chi_s(1) \rangle] \\
\langle \chi_r(1)|\hat{K}(1)|\chi_s(1) \rangle &= \sum_{b=1}^{b} \sum_{u=1}^{b} c_{ru}^s c_{wu}^s \\
\langle \chi_r(1)|\hat{J}(1)|\chi_s(1) \rangle &= \sum_{r=1}^{b} \sum_{u=1}^{b} c_{rs}^s c_{ru}^s

F_{rs} &= H_{rs}^{\text{core}} + \sum_{b=1}^{b} \sum_{u=1}^{b} \sum_{j=1}^{n/2} c_{ji}^s c_{uj}^s [2\langle rs|tu \rangle - \langle ru|ts \rangle]

F_{rs} &= H_{rs}^{\text{core}} + \sum_{b=1}^{b} \sum_{u=1}^{b} \sum_{t=1}^{b} \sum_{u=1}^{b} P_{tu} [(rs|tu) - \frac{1}{2}(ru|ts)]

H_{rs}^{\text{core}} &= \langle \chi_r(1)|\hat{H}^{\text{core}}(1)|\chi_s(1) \rangle

P_{tu} &= 2 \sum_{j=1}^{n/2} c_{ji}^s c_{uj}^s, \quad t = 1, 2, \ldots, b, \quad u = 1, 2, \ldots, b

density (charge, bond-order) matrix elements

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\[ \rho = 2 \sum_{j=1}^{n/2} \phi_j^* \phi_j \]

\[ \phi_j = \sum_{r=1}^b c_{ir} \chi_r \]

\[ = 2 \sum_{r=1}^b \sum_{s=1}^b \sum_{j=1}^{n/2} c_{ir}^* c_{sj} \chi_r^* \chi_s \]

\[ P_{rs} = 2 \sum_{j=1}^{n/2} c_{ir}^* c_{sj} \]

\[ = \sum_{r=1}^b \sum_{s=1}^b P_{rs} \chi_r^* \chi_s \]

\[ E_{HF} = 2 \sum_{i=1}^{n/2} e_i - \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (2J_{ij} - K_{ij}) + V_{NN} \]

\[ = \sum_{i=1}^{n/2} e_i + \sum_{i=1}^{n/2} H_{ii}^{\text{core}} + \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (2J_{ij} - K_{ij}) \]

\[ H_{ii}^{\text{core}} = \langle \phi_i | H_{ii}^{\text{core}} | \phi_i \rangle = \sum_s c_{is}^* c_{is} \langle \chi_i | H_{ii}^{\text{core}} | \chi_i \rangle = \sum_s c_{is}^* c_{is} H_{ii}^{\text{core}} \]

\[ E_{HF} = \sum_{i=1}^{n/2} e_i + \sum_{r=1}^b \sum_{s=1}^b c_{ir}^* c_{sr} H_{rs}^{\text{core}} + V_{NN} \]

\[ E_{HF} = \sum_{i=1}^{n/2} e_i + \frac{1}{2} \sum_{r=1}^b \sum_{s=1}^b P_{rs} H_{rs}^{\text{core}} + V_{NN} \]
\[ \hat{F} \phi_i = \epsilon_i \phi_i \]

\[ \epsilon_i = \langle \phi_i | \hat{F} | \phi_i \rangle \]

\[ \phi_i = \sum_{s=1}^{b} c_{s} \chi_s \]

\[ \epsilon_i = \sum_r \sum_s c_{ri}^* c_{si} \langle \chi_r | \hat{F} | \chi_s \rangle = \sum_r \sum_s c_{ri}^* c_{si} F_{rs} \]

\[ \sum_r \epsilon_i = \sum_r \sum_s \sum_i c_{ri}^* c_{si} F_{rs} = \frac{1}{2} \sum_r \sum_s P_{rs} F_{rs} \]

\[ E_{HF} = \sum_{i=1}^{n/2} \epsilon_i + \frac{1}{2} \sum_{r=1}^{b} \sum_{s=1}^{b} P_{rs} H_{rs}^{\text{core}} + V_{NN} \]

\[ \sum_r \epsilon_i = \sum_r \sum_s \sum_i c_{ri}^* c_{si} F_{rs} = \frac{1}{2} \sum_r \sum_s P_{rs} F_{rs} \]

\[ E_{HF} = \frac{1}{2} \sum_{r=1}^{b} \sum_{s=1}^{b} P_{rs} (F_{rs} + H_{rs}^{\text{core}}) + V_{NN} \]
EXAMPLE Do an SCF calculation for the helium-atom ground state using a basis set of two 1s STOs with orbital exponents $\zeta_1 = 1.45$ and $\zeta_2 = 2.91$.

normalized basis functions:

\[
\chi_1 = 2\zeta_1^{1/2}e^{-\zeta_1 r}Y_0^0, \quad \chi_2 = 2\zeta_2^{1/2}e^{-\zeta_2 r}Y_0^0, \quad \zeta_1 = 1.45, \quad \zeta_2 = 2.91
\]

We solve the Roothaan equations:

\[
\begin{align*}
S_{11} &= \langle \chi_1 | \chi_1 \rangle = 1, \quad S_{22} = \langle \chi_2 | \chi_2 \rangle = 1 \\
S_{12} &= S_{21} = \langle \chi_1 | \chi_2 \rangle = 4\zeta_1^{3/2}\zeta_2^{3/2} \int_0^{\infty} e^{-\zeta_1 r} e^{-\zeta_2 r} r^2 dr = \frac{8\zeta_1^{3/2}\zeta_2^{3/2}}{(\zeta_1 + \zeta_2)^3} = 0.8366
\end{align*}
\]

\[
H_{11}^{\text{core}} = \langle \chi_1 | \hat{H}^{\text{core}} | \chi_1 \rangle \\
\hat{H}^{\text{core}} = -\frac{1}{2} \nabla^2 - 2/r = -\frac{1}{2} \nabla^2 - \zeta/r + (\zeta - 2)/r
\]

\[
\begin{align*}
H_{11}^{\text{core}} &= \langle \chi_1 | \hat{H}^{\text{core}} | \chi_1 \rangle = -\frac{1}{2} \zeta_1^2 + (\zeta_1 - 2) \zeta_1 = \frac{1}{2} \zeta_1^2 - 2 \zeta_1 = -1.8488 \\
H_{22}^{\text{core}} &= \frac{1}{2} \zeta_2^2 - 2 \zeta_2 = -1.5860 \\
H_{12}^{\text{core}} &= H_{21}^{\text{core}} = \langle \chi_1 | \hat{H}^{\text{core}} | \chi_2 \rangle = -\frac{1}{2} \zeta_2^2 S_{12} + \frac{4(\zeta_2 - 2) \zeta_1^{3/2} \zeta_2^{3/2}}{(\zeta_1 + \zeta_2)^3} \\
&= \frac{\zeta_1^{3/2} \zeta_2^{3/2} (4 \zeta_1 \zeta_2 - 8 \zeta_1 - 8 \zeta_2)}{(\zeta_1 + \zeta_2)^3} = -1.8826
\end{align*}
\]

\[
(rs|tu) = (sr|ut) = (sr|ut) = (tu|rs) = (ut|rs) = (ut|sr)
\]
To start the calculation

\[ (1|1) = |\zeta_1| = 0.9062, \quad (2|2) = |\zeta_3| = 1.1888 \]
\[ (1|2) = (2|1) = \left( \zeta_1^2 \zeta_2 + 4\zeta_1^2 \zeta_3 + 9\zeta_2^2 \zeta_3 \right) / (|\zeta_1|^2 + |\zeta_3|^2) = 1.1826 \]
\[ (1|2) = (2|1) = (1|2) = (2|1) = 20\zeta_1^2 \zeta_3^2 / (|\zeta_1|^2 + |\zeta_3|^2) = 0.9536 \]
\[ (1|2) = (1|2) = (1|2) = (2|2) = (1|2) = (2|2) = 0.9033 \]
\[ (2|2) = (2|2) = (2|2) = (2|2) = 1.2980 \]

For normalization condition:

\[ c_{21} = (1 + k^2 + 2kS_{12})^{-1/2}, \quad \text{where} \quad k = c_{12}/c_{21} \]

Substitution of \( k = 2 \) and \( S_{12} = 0.8366 \) gives \( c_{21} \approx 0.3461 \) and \( c_{11} = 2c_{21} = 0.6922 \). With \( n = 2 \) and \( b = 2 \)

\[ P_{11} = 2c_{11}^2 c_{12}, \quad P_{12} = 2c_{11} c_{21}, \quad P_{21} = P_{21}^*, \quad P_{22} = 2c_{21}^2 c_{21} \]

\[ c_{21} = 0.3461 \] and \( c_{11} = 2c_{21} = 0.6922 \)

\[ P_{11} \approx 0.9583, \quad P_{12} = P_{21} \approx 0.4791, \quad P_{22} \approx 0.2396 \]
The initial estimate of the secular equation:

\[
\begin{vmatrix}
-0.813 - \varepsilon_i & -0.892 - 0.8366\varepsilon_i \\
-0.892 - 0.8366\varepsilon_i & 0.070 - \varepsilon_i
\end{vmatrix} = 0
\]

\[0.3001\varepsilon_i^2 - 0.6095\varepsilon_i - 0.739 \approx 0\]

\[\varepsilon_1 = -0.854, \quad \varepsilon_2 = 2.885\]

lower root \(\varepsilon_1\) into the Roothaan equation

\[c_{11}(F_{21} - \varepsilon_1 S_{21}) + c_{21}(F_{22} - \varepsilon_1 S_{22}) = 0\]

\[-0.1777c_{11} + 0.784c_{21} = 0\]

\[c_{11}/c_{21} \approx 4.42\]

Substitution of \(k = 4.42\) and \(S_{12} = 0.8366\) in the normalization condition

\[c_{21} = 0.189, \quad c_{11} = kc_{21} = 0.836\]

improved coefficients

\[F_{11} = H_{11}^{\text{core}} + \frac{1}{2}P_{11}(11)[11] + P_{12}(11)[12] + P_{22}(11)[22] - \frac{1}{2}(12[21])\]

\[F_{12} = F_{21} = H_{12}^{\text{core}} + \frac{1}{2}P_{12}(12)[11] + P_{21}(12)[12] - \frac{1}{2}(11[22]) + \frac{1}{2}P_{22}(12)[22]\]

\[F_{22} = H_{22}^{\text{core}} + P_{11}(22)[11] - \frac{1}{2}(21[12]) + P_{21}(22)[12] + \frac{1}{2}P_{22}(22)[22]\]

values of the \(H_n^{\text{core}}\) and \((rs|tu)\) integrals

\[F_{11} \approx -1.8488 + 0.4531P_{11} + 0.9033P_{12} + 0.7058P_{22}\]

\[F_{12} = F_{21} = -1.8826 + 0.4516P_{11} + 0.8391P_{12} + 0.6490P_{22}\]

\[F_{22} = -1.5860 + 0.7058P_{11} + 1.2980P_{12} + 0.9094P_{22}\]

\[P_{11} \approx 0.9583, \quad P_{12} = P_{21} = 0.4791, \quad P_{22} \approx 0.2396\]

\[F_{11} \approx -0.813, \quad F_{12} = F_{21} = -0.892, \quad F_{22} = -0.070\]
Another cycle gives:

\[
P_{11} = 1.418, \quad P_{12} = P_{21} = 0.308, \quad P_{22} = 0.067
\]

\[
F_{11} = -0.881, \quad F_{12} = F_{21} = -0.940, \quad F_{22} = -0.124_{6}
\]

\[
\varepsilon_1 \approx -0.918, \quad \varepsilon_2 = 2.809
\]

\[
c_{11} \approx 0.842, \quad c_{21} = 0.183
\]

\(c_1\)'s are the same as those for the previous cycle (converged).

SCF energy (with \(n = 2\) and \(b = 2\)):

\[
E_{HF} = -0.918 + \frac{1}{2}[1.418(-1.8488) + 2(0.308)(-1.8826) + 0.067(-1.5860)] + 0
\]

\[= -2.862 \text{ hartrees} = -77.9 \text{ eV}\]
**Matrix Form of the Roothaan Equations**

The Roothaan equations are most efficiently solved using matrix methods.

\[
\sum_{s=1}^{b} F_{rs} c_{si} = \sum_{s=1}^{b} S_{rs} c_{si} \varepsilon_{i}, \quad r = 1, 2, \ldots, b
\]

- \( c_{si} \): relate the MOs \( \phi_i \) to \( \chi_s \)
- \( \phi_i = \sum_s c_{si} \chi_s \)
- \( F_{rs} = \langle \chi_r | \hat{F} | \chi_s \rangle \)
- \( S_{rs} = \langle \chi_r | \chi_s \rangle \)
- \( \varepsilon_i \): orbital energies

Use of the matrix multiplication rule:

\[ (\mathbf{C} \varepsilon)_{si} = \sum_m c_{sm} \varepsilon_{mi} = \sum_m c_{sm} \delta_{mi} \varepsilon_i = c_{si} \varepsilon_i \]

\[
\sum_{s=1}^{b} F_{rs} c_{si} = \sum_{s=1}^{b} S_{rs} (\mathbf{C} \varepsilon)_{si}
\]

**C**: be the square matrix of order \( b \) whose elements are the coefficients \( c_{si} \)

**F**: be the square matrix of order \( b \) whose elements are

**S**: be the square matrix whose elements are

**\( \varepsilon \)**: be the diagonal square matrix whose diagonal elements are the orbital energies \( \varepsilon_{1}, \varepsilon_{2}, \varepsilon_{3}, \ldots \) orbital energies

\[ \varepsilon_{mi} = \delta_{mi} \varepsilon_i \]

\[
\sum_{s=1}^{b} (\mathbf{F} \varepsilon)_{si} = \sum_{s=1}^{b} (S_{rs}(\mathbf{C} \varepsilon))_{si}
\]

\( (r, i) \)th element of **FC**  \( (r, i) \)th element of **S(C \varepsilon)**

\[
\mathbf{FC} = \mathbf{SC} \varepsilon
\]

*matrix form of the Roothaan equations.*
The set \( \{\chi_s\} \) is not an orthogonal set. Schmidt or some other procedure: linear combinations of the basis functions.

\[ \chi'_i = \sum_i a_{is} \chi_i \quad S'_{ij} = \langle \chi'_i | \chi'_j \rangle = \delta_{ij} \]

See Szabo and Ostlund, Section 3.4.5, for details of the orthogonalization in \( \{\chi'_s\} \) the overlap matrix is a unit matrix: \( S'_{ij} = \langle \chi'_i | \chi'_j \rangle = \delta_{ij} \).

\[ FC = SC \epsilon \quad \rightarrow \quad F'C' = C' \epsilon \]

\[ F'_{ij} = \langle \chi'_i | \tilde{F} | \chi'_j \rangle \]

\( C' \) : relate the MOs \( \phi_i \) to the orthonormal BFs: \( \phi_i = \sum_i c_{i}^{\dagger} \chi_i \)

\( F' \) and \( C' \) are readily calculated from \( F \) and \( C \).

\( F \) and \( F' \) matrices and the \( C \) and \( C' \) matrices are related by (Problem 8.49c):

\[ F' = A' FA \quad \text{and} \quad C = AC' \]

where \( A \) is the matrix of coefficients \( a_{is} \) in \( \chi'_i = \sum_i a_{is} \chi_i \).

\[ F'C' = C' \epsilon \]

The orbital energies \( \epsilon_i \) are the eigenvalues of the Fock matrix \( F' \) and each column of \( C' \) is an eigenvector of \( F' \).

- \( F \) is Hermitian \( \iff \) \( F' \) is a Hermitian matrix
- its inverse equals its conjugate transpose \( C'^{-1} = C'^{\dagger} \)
- the eigenvector matrix \( C' \) can be chosen to be unitary
- the MOs \( \phi_i \) are orthonormal

\[ F'C' = C' \epsilon \]

Multiplication on the left by \( C'^{-1} = C'^{\dagger} \)

\[ C'^{-1} F'C' = \epsilon \]
For an SCF calculation at a specified molecular geometry:

1. Choose a basis set \( \chi_b \).
2. Evaluate the \( H_{ij}^{\text{corr}} \), \( S_{ij} \), and \( \langle rs | tu \rangle \) integrals.
3. Use the overlap integrals \( S_{ij} \) and an orthogonalization procedure to calculate the \( \mathbf{A} \) matrix of coefficients \( a_{ij} \) that will produce orthonormal basis functions \( \chi_{ji} = \sum_{t} a_{jt} \chi_t \).
4. Make an initial guess for the coefficients \( c_{ij} \) in the MOs \( \phi_i = \sum_{s} c_{is} \chi_s \). From the initial guess of coefficients, calculate the density matrix \( \mathbf{P} \) in

\[
P_{iu} = 2 \sum_{j=1}^{n/2} c_{ij}^* c_{uj}, \quad t = 1, 2, \ldots, b, \quad u = 1, 2, \ldots, b
\]

5. Use

\[
E_s = H_{ij}^{\text{corr}} + \sum_{r=1}^{b} \sum_{\tau=1}^{b} P_{ru} \langle rs | tu \rangle - \frac{1}{2} \langle ru | rs \rangle
\]

to calculate an estimate of the Fock matrix elements \( F_{rs} \) from \( \mathbf{P} \) and the \( \langle rs | tu \rangle \) and \( H_{ij}^{\text{corr}} \) integrals.
6. Calculate the matrix \( \mathbf{F} \) using \( \mathbf{F} = \mathbf{A}^\dagger \mathbf{F} \mathbf{A} \).

7. Use a matrix-diagonalization method to find the eigenvalue and eigenvector matrices \( \mathbf{e} \) and \( \mathbf{C} \) of \( \mathbf{F} \).
8. Calculate the coefficient matrix \( \mathbf{C} = \mathbf{A} \mathbf{C} \).
9. Calculate an improved estimate of the density matrix from \( \mathbf{C} \) using \( \mathbf{P} = 2 \mathbf{C} \mathbf{C}^\dagger \), which is the matrix form of

\[
P_{iu} = 2 \sum_{j=1}^{n/2} c_{ij}^* c_{uj}, \quad t = 1, 2, \ldots, b, \quad u = 1, 2, \ldots, b
\]

10. Compare the improved \( \mathbf{P} \) with the preceding estimate of \( \mathbf{P} \). If the differences are negligible, the calculation has converged and one uses the converged SCF wave function to calculate molecular properties. If the calculation has not converged, one goes back to step (5).
To find the equilibrium geometry of a molecule, one does a series of SCF calculations at many successive geometries. For the second and later SCF calculations of the series, one takes the initial guess of \( P \) as \( P \) for the SCF wave function of a nearby geometry.

1) One way to begin an SCF calculation:

\[
F_{\text{rel}} = H_{\text{rel}}^{\text{core}} + \sum_{r,s} \sum_{u=1}^B P_{ru} \left[ (r,s|u) - \frac{1}{2} (u|s)r \right] \rightarrow F_{\text{rel}} \approx H_{\text{rel}}^{\text{core}}
\]

2) ab initio SCF calculations get the initial estimate of the density matrix by doing a semiempirical calculation on the molecule.

3) a guess for the \( P \) matrix by using the density matrices of the atoms composing the molecule.

THE VIRIAL THEOREM

two theorems aid in understanding chemical bonding.

\[
\hat{H} \psi = E \psi
\]

\[ \hat{\Delta} \] be a linear, time-independent operator.

\[
\int \psi^{*} [ \hat{H}, \hat{\Delta} ] \psi \, d \tau = \langle \psi | \hat{H} \hat{\Delta} - \hat{\Delta} \hat{H} \psi \rangle = \langle \psi | \hat{H} \hat{\Delta} \psi \rangle - E \langle \psi | \hat{\Delta} \psi \rangle
\]

\[
\langle \psi | \hat{H} \hat{\Delta} \psi \rangle = \langle \hat{\Delta} \psi | \hat{H} \psi \rangle^* = E \langle \hat{\Delta} \psi | \psi \rangle^* = E \langle \psi | \hat{\Delta} \psi \rangle = E \langle \psi | \hat{\Delta} \psi \rangle
\]

\[
\int \psi^{*} [ \hat{H}, \hat{\Delta} ] \psi \, d \tau = 0
\]

hypervirial theorem.

does not apply to continuum stationary states
derive the virial theorem:

We choose

\[ \hat{A} = \sum_i \hat{q}_i \hat{p}_i = -i \hbar \sum_i q_i \frac{\partial}{\partial q_i} \]

over the 3n Cartesian coordinates of the n particles.

Cartesian coordinates: \( q_1, q_2, q_3, \ldots \)
linear-momentum components \( p_1, p_2, p_3, \ldots \)

\[
\begin{align*}
[\hat{H}, \hat{A}] & = \sum_i [\hat{H}, \hat{q}_i \hat{p}_i] = \sum_i \hat{q}_i [\hat{H}, \hat{p}_i] + \sum_i [\hat{H}, \hat{q}_i] \hat{p}_i \\
& = i\hbar \sum_i q_i \frac{\partial V}{\partial q_i} - i\hbar \sum_i \frac{1}{m_i} \hat{p}_i^2 = i\hbar \sum_i q_i \frac{\partial V}{\partial q_i} - 2i\hbar \hat{T}
\end{align*}
\]

\( \hat{T} \) and \( \hat{V} \) are the kinetic- and potential-energy operators

\[
\langle \psi \left| \sum_i q_i \frac{\partial V}{\partial q_i} \right| \psi \rangle = 2 \langle \psi \left| \hat{T} \right| \psi \rangle
\]

virial theorem
is restricted to bound stationary states
A function \( f(x_1, x_2, ..., x_j) \) of several variables is homogeneous of degree \( n \) if it satisfies:

\[
f(sx_1, sx_2, ..., sx_j) = s^nf(x_1, x_2, ..., x_j)
\]

Example:

\[
g = \frac{1}{x^3} + \frac{1}{y^3} + \frac{x}{y^2z^2} \quad \text{homogeneous of degree -3}
\]

\[
g(sx, sy, sz) = \frac{1}{s^3x^3} + \frac{1}{s^3y^3} + \frac{1}{s^3z^3} + \frac{sx}{s^3y^3z^2} = s^{-3}g(x, y, z)
\]

**Euler’s theorem**: if \( f(x_1, x_2, ..., x_j) \) is homogeneous of degree \( n \), then

\[
\sum_{k=1}^{j} x_k \frac{\partial f}{\partial x_k} = nf
\]

**Exercise**: Prove the Euler’s theorem.

if \( f(x_1, x_2, ..., x_j) \) is homogeneous of degree \( n \), then

\[
f(sx_1, sx_2, ..., sx_j) = s^nf(x_1, x_2, ..., x_j)
\]

Let

\[
u_1 = sx_1, \quad u_2 = sx_2, \quad ..., \quad u_j = sx_j
\]

\[
\frac{\partial f(u_1, ..., u_j)}{\partial s} = \frac{\partial f}{\partial u_1} \frac{\partial u_1}{\partial s} + \frac{\partial f}{\partial u_2} \frac{\partial u_2}{\partial s} + ... + \frac{\partial f}{\partial u_j} \frac{\partial u_j}{\partial s}
\]

\[
= x_1 \frac{\partial f}{\partial u_1} + x_2 \frac{\partial f}{\partial u_2} + ... + x_j \frac{\partial f}{\partial u_j} = \sum_{k=1}^{j} x_k \frac{\partial f}{\partial u_k}
\]

\[
s^{n-1}f(x_1, ..., x_j) = \sum_{k=1}^{j} x_k \frac{\partial f(u_1, ..., u_j)}{\partial u_k}
\]

Let \( s = 1 \), so that \( u_i = x_i \) completes the proof.
If $V$ is a homogeneous function of degree $n$ when expressed in Cartesian coordinates:

$$\sum_{k=1}^{l} x_k \frac{\partial f}{\partial x_k} = nf \quad \Rightarrow \quad \sum_{i} q_i \frac{\partial V}{\partial q_i} = nV$$

$$\langle \sum_{i} q_i \frac{\partial V}{\partial q_i} \rangle = 2\langle T \rangle \quad \Rightarrow \quad \sum_{i} q_i \frac{\partial V}{\partial q_i} = nV$$

**EXAMPLE**

Apply the virial theorem to (a) the one-dimensional harmonic oscillator; (b) the hydrogen atom; (c) a many-electron atom.

a) $V = \frac{1}{2}kx^2$

$$2\langle T \rangle = n\langle V \rangle \quad \Rightarrow \quad \langle T \rangle = \langle V \rangle = \frac{1}{2}E = \frac{1}{2}\hbar \nu (\nu + \frac{1}{2})$$

b) $V = -e^2/(x^2 + y^2 + z^2)^{1/2}$

$$2\langle T \rangle = n\langle V \rangle \quad \Rightarrow \quad \langle T \rangle = -\langle V \rangle$$

c) $V = -Ze^2 \sum_{i=1}^{n} \frac{1}{(x_i^2 + y_i^2 + z_i^2)^{1/2}} + \sum_{j>i}^{n} \frac{e^2}{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}^{1/2}$

$$2\langle T \rangle = n\langle V \rangle \quad \Rightarrow \quad \langle T \rangle = -\langle V \rangle$$
Molecules:

\[ \psi = \psi_{\text{el}}(q; q_a) \psi_N(q_a) \]

In the Born-Oppenheimer approximation

\[ \hat{H}_{\text{el}} \psi_{\text{el}}(q; q_a) = E_{\text{el}}(q_a) \psi_{\text{el}}(q; q_a) \]

electronic Schrödinger equation

\[ E_{\text{el}}: \text{electronic energy} \]

\[ \hat{H}_{\text{el}} = \hat{T}_{\text{el}} + \hat{V}_{\text{el}} \]

\[ \hat{T}_{\text{el}} = -\frac{\hbar^2}{2m_e} \sum_i \left( \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) \]

\[ \hat{V}_{\text{el}} = -\sum_a \sum_i \frac{Z_a e^2}{\sqrt{[(x_i - x_a)^2 + (y_i - y_a)^2 + (z_i - z_a)^2]^{1/2}}} \]

\[ + \sum_i \sum_{j>i} \frac{e^2}{\sqrt{[(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{1/2}}} \]

Let the system be in the electronic stationary state \( \psi_{\text{el}} \)

\[ \psi_{\text{el}}(q; q_a; q_a) \]

being parameters

the virial theorem is seen to be valid for the electronic kinetic- and potential-energy operators:

\[ 2\langle \psi_{\text{el}} | \hat{T}_{\text{el}} | \psi_{\text{el}} \rangle = \langle \psi_{\text{el}} | \sum_i q_i \frac{\partial \hat{V}_{\text{el}}}{\partial q_i} | \psi_{\text{el}} \rangle \]

\( V_{\text{el}} \) (as a function of electronic coordinates, ) is not a homogeneous function:

\[ \sqrt{[(sx_i - x_a)^2 + (sy_i - y_a)^2 + (sz_i - z_a)^2]^{-1/2}} \neq s^{-1}\sqrt{[(x_i - x_a)^2 + (y_i - y_a)^2 + (z_i - z_a)^2]^{-1/2}} \]

the virial theorem for \( <T_{\text{el}} > \) and \( <V_{\text{el}} > \) of a molecule will not have a simple form
$V_{el}$ (as a function of both the electronic and the nuclear Cartesian coordinates) is a homogeneous function of degree -1

$$[(sx_i - sx_a)^2 + (sy_i - sy_a)^2 + (sz_i - sz_a)^2]^{-1/2} = s^{-1}[(x_i - x_a)^2 + (y_i - y_a)^2 + (z_i - z_a)^2]^{-1/2}$$

$$\sum_{k=1}^{j} x_k \frac{\partial f}{\partial x_k} = nf \quad \rightarrow \quad \sum_{i} q_i \frac{\partial V_{el}}{\partial q_i} + \sum_{\alpha} q_{\alpha} \frac{\partial V_{el}}{\partial q_{\alpha}} = -V_{el}$$

Euler’s theorem

$$2\langle \psi_{el} | \hat{T}_{el} | \psi_{el} \rangle = \left\langle \psi_{el} \left| \sum_{i} q_i \frac{\partial V_{el}}{\partial q_i} \right| \psi_{el} \right\rangle$$

$$\sum_{i} q_i \frac{\partial V_{el}}{\partial q_i} + \sum_{\alpha} q_{\alpha} \frac{\partial V_{el}}{\partial q_{\alpha}} = -V_{el}$$

$$2\langle \psi_{el} | \hat{T}_{el} | \psi_{el} \rangle = -\langle \psi_{el} | V_{el} | \psi_{el} \rangle - \left\langle \psi_{el} \left| \sum_{\alpha} q_{\alpha} \frac{\partial V_{el}}{\partial q_{\alpha}} \right| \psi_{el} \right\rangle$$

additional term

$$2\langle \psi_{el} | \hat{T}_{el} | \psi_{el} \rangle = -\langle \psi_{el} | V_{el} | \psi_{el} \rangle - \left\langle \psi_{el} \left| \sum_{\alpha} q_{\alpha} \frac{\partial V_{el}}{\partial q_{\alpha}} \right| \psi_{el} \right\rangle$$

$$\left\langle \psi_{el} \left| \sum_{\alpha} q_{\alpha} \frac{\partial V_{el}}{\partial q_{\alpha}} \right| \psi_{el} \right\rangle = \sum_{\alpha} q_{\alpha} \int \psi_{el}^{*} \frac{\partial V_{el}}{\partial q_{\alpha}} \psi_{el} d\tau_{el}$$

$$\int \psi_{el}^{*} \frac{\partial V_{el}}{\partial q_{\alpha}} \psi_{el} d\tau_{el} = \frac{\partial E_{el}}{\partial q_{\alpha}}$$

we shall show

an example of the Hellmann-Feynman theorem

$$2\langle \psi_{el} | \hat{T}_{el} | \psi_{el} \rangle = -\langle \psi_{el} | V_{el} | \psi_{el} \rangle - \sum_{\alpha} q_{\alpha} \frac{\partial E_{el}}{\partial q_{\alpha}}$$

eliminate either $<T_{el}>$ or $<V_{el}>$
Consider a diatomic molecule:
\[ E_{el} = E_{el}(R) \]

\[ \frac{\partial E_{el}}{\partial x_a} = \frac{dE_{el}}{dR} \frac{\partial R}{\partial x_a}, \quad \frac{\partial E_{el}}{\partial y_a} = \frac{dE_{el}}{dR} \frac{\partial R}{\partial y_a}, \quad \frac{\partial E_{el}}{\partial z_a} = \frac{dE_{el}}{dR} \frac{\partial R}{\partial z_a} \]

\[ R = \left[ (x_a - x_b)^2 + (y_a - y_b)^2 + (z_a - z_b)^2 \right]^{1/2} \]

\[ \frac{\partial R}{\partial x_a} = \frac{x_a - x_b}{R}, \quad \frac{\partial R}{\partial y_a} = \frac{y_a - y_b}{R}, \quad \frac{\partial R}{\partial z_a} = \frac{z_a - z_b}{R} \]

similar equations for the y and z

\[ \sum_a q_a \frac{\partial E_{el}}{\partial q_a} = \frac{1}{R} \frac{dE_{el}}{dR} \left[ x_a(x_a - x_b) + y_a(y_a - y_b) + z_a(z_a - z_b) \right] + \frac{dE_{el}}{dR} \]

\[ \sum_a q_a \frac{\partial E_{el}}{\partial q_a} = R \frac{dE_{el}}{dR} \]

for a diatomic molecule becomes

\[ 2\langle T_e \rangle = -\langle V_{el} \rangle - \sum_a q_a \frac{\partial E_{el}}{\partial q_a} \]

\[ \sum_a q_a \frac{\partial E_{el}}{\partial q_a} = R \frac{dE_{el}}{dR} \]

\[ 2\langle T_e \rangle = -\langle V_{el} \rangle - R \frac{dE_{el}}{dR} \]

\[ \langle T_{el} \rangle + \langle V_{el} \rangle = E_{el} \]

\[ \langle T_{el} \rangle = -E_{el} - R \frac{dE_{el}}{dR} \]

\[ \langle V_{el} \rangle = 2E_{el} + R \frac{dE_{el}}{dR} \]
Do not omit the internuclear repulsion:

\[ V_{NN} = \sum_{\beta} \sum_{\alpha > \beta} \frac{Z_{\alpha}Z_{\beta}e^2}{[x_{\alpha} - x_{\beta}]^2 + (y_{\alpha} - y_{\beta})^2 + (z_{\alpha} - z_{\beta})^2]^{1/2}} \]

\[ V = V_{el} + V_{NN} \]

\( \hat{T}_{el} + \hat{V} \psi_{el} = U(q_a) \psi_{el} \) electronic Schrodinger equation

\[ U(q_a) = E_{el}(q_a) + V_{NN} \]

\[-\int \psi_{el}^* (\hat{V}_{el} + V_{NN}) \psi_{el} d\tau_{el} = -\sum_a q_a \frac{\partial U}{\partial q_a} \]

\[ = -\langle \psi_{el} | \hat{V}_{el} | \psi_{el} \rangle - V_{NN} - \sum_a q_a \frac{\partial E_{el}}{\partial q_a} - \sum_a q_a \frac{\partial V_{NN}}{\partial q_a} \]

\[ V_{NN} \text{ is a homogeneous function of the nuclear Cartesian coordinates of degree } -1: \]

\[ \sum_a q_a \frac{\partial V_{NN}}{\partial q_a} = -V_{NN} \]

\[-\langle \psi_{el} | \hat{V}_{el} + V_{NN} | \psi_{el} \rangle - \sum_a q_a \frac{\partial U}{\partial q_a} = -\langle \psi_{el} | \hat{V}_{el} | \psi_{el} \rangle - \sum_a q_a \frac{\partial E_{el}}{\partial q_a} \]

\[ 2\langle T_{el} \rangle = -\langle V_{el} \rangle - \sum_a q_a \frac{\partial E_{el}}{\partial q_a} \]

\[ = -\langle \psi_{el} | \hat{V}_{el} + V_{NN} | \psi_{el} \rangle - \sum_a q_a \frac{\partial U}{\partial q_a} = -\langle \psi_{el} | \hat{V}_{el} | \psi_{el} \rangle - \sum_a q_a \frac{\partial E_{el}}{\partial q_a} \]

\[ 2\langle T_{el} \rangle = -\langle V \rangle - \sum_a q_a \frac{\partial U}{\partial q_a} \]

\[ = -\langle \psi_{el} | \hat{V}_{el} + V_{NN} | \psi_{el} \rangle - \sum_a q_a \frac{\partial U}{\partial q_a} \]

\[ 2\langle T_{el} \rangle = -\langle V \rangle - R(dU/dR) \]

\[ \langle T_{el} \rangle = - U - R(dU/dR) \]

\[ \langle V \rangle = 2U + R(dU/dR) \]

(potential energy) \( V = V_{el} + V_{NN} = 0 \) where all particles at infinite separation \( R \to \infty \) \( \Rightarrow U(R) \to 0 \) (\( \sum E_{\text{separated atoms}} \) which is negative)
For diatomic molecules:

\[ 2(T_{\text{el}}) = -\langle V \rangle - \sum_a \frac{\partial U}{\partial q_a} \]

For polyatomic molecules:

\[ 2(T_{\text{el}}) = -\langle V \rangle - \sum_a \sum_{\beta \neq a} R_{\alpha \beta} \left( \frac{\partial U}{\partial R_{\alpha \beta}} \right) \]

over either all internuclear distances or the bond lengths only

The true wave functions with $V$ a homogeneous function of the coordinates must satisfy this form of the virial theorem:

\[ 2\langle T \rangle = n\langle V \rangle \]

What about an approximate wave function?

by inserting a variational parameter as a multiplier of each Cartesian coordinate (nuclear coordinates for molecules and electronic coordinates for atoms) and choosing this parameter to minimize the variational integral, we can make any trial variation function satisfy the virial theorem (is called scaling; variational parameter ≡ scale factor).

1) $\psi^{(0)}$ for the heliumlike atom has no scale factor and so does not satisfy the virial theorem.

\[ \psi_{1s}^{(0)} = \frac{1}{\pi^{1/2}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}, \quad \frac{1}{\pi^{1/2}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0} = 1s(1)1s(2) \]

2) The Heitler-London trial function for $H_2$ has no scale factor and does not satisfy the virial theorem.

\[ \frac{1s(1)1s(2) + 1s(2)1s(1)}{\sqrt{2(1 + S_{ab})^{1/2}}} \frac{1}{\sqrt{2}} \left[ \alpha(1)\beta(2) - \alpha(2)\beta(1) \right] \]

3) The Heitler-London-Wang function, which uses a variationally determined orbital exponent ($\zeta$), satisfies the virial theorem.

4) Hartree-Fock wave functions satisfy the virial theorem; because of scale factor in the Slater basis functions.

\[ \frac{(2\zeta/a_0)^{n+1/2}}{[2(n)!]^{1/2}} r^n e^{-r/\alpha} Y_n^m(\theta, \phi) \]
THE VIRIAL THEOREM AND CHEMICAL BONDING

Use the virial theorem to examine the changes in $T_{el}$ and $V$ that occur when a covalent chemical bond is formed in a diatomic molecule.

For a stable bond:

At $R = \infty$ (we have the separated atoms):

- $2\langle T_{el} \rangle_{\infty} = -\langle V \rangle_{\infty}$
- $\langle T_{el} \rangle_{\infty} = -U(\infty)$
- $\langle V \rangle_{\infty} = 2U(\infty)$

the sum of the energies of the two separated atoms

Thus:

- $2\langle T_{el} \rangle = -\langle V \rangle - R(dU/dR)$
- $\langle T_{el} \rangle = -U - R(dU/dR)$
- $\langle V \rangle = 2U + R(dU/dR)$

$\langle T_{el} \rangle_{R_e} = -\langle U \rangle_{R_e}$
$\langle V \rangle_{R_e} = 2U(R_e)$

resemble those for atoms
\[ \langle T_e \rangle_R = -U(R_e) \]
\[ \langle T_e \rangle_\infty = -U(\infty) \]
\[ \langle V \rangle_R = 2U(R_e) \]
\[ \langle V \rangle_\infty = 2U(\infty) \]
\[ \langle V \rangle_R - \langle V \rangle_\infty = 2[U(R_e) - U(\infty)] \]

The sum of \( V \) of the separated atoms

For bonding, we have \( U(\text{bond}) < U(\infty) \):
\[ \langle V \rangle_R < \langle V \rangle_\infty \]
\[ \langle T_e \rangle_R > \langle T_e \rangle_\infty \]

decrease in \( V \) = \( 2 \times \) increase in \( T_{el} \)

Why?
electrons feel the attractions of both nuclei and (perhaps) orbital exponents increase in the molecule

- equilibrium dissociation energy:
  \[ D_e = \frac{1}{2} [\langle V \rangle_\infty - \langle V \rangle_R] \]

behavior of the \( \langle V \rangle \) and \( \langle T_{el} \rangle \) for large \( R \):
van der Waals forces (vdWf): interactions between atoms at large \( R \).
For two neutral atoms, at least one of which is in an S state, QM perturbation theory shows:

\[ \text{vdW-force} \propto \frac{1}{R^7} \]

and
\[ U(R) = U(\infty) - \frac{A}{R^6}, \quad R \text{ large} \]

\( A \): a positive constant.

vdWf between neutral atoms are called \textbf{London forces} or \textbf{dispersion forces}.

\[ \langle T_{el} \rangle = -U - R(dU/dR) \]
\[ \langle V \rangle = 2U + R(dU/dR) \]
\[ \langle T_{el} \rangle \approx \langle T_{el} \rangle_\infty - \frac{5A}{R^6}, \quad R \text{ large} \]
\[ \langle V \rangle \approx \langle V \rangle_\infty + \frac{4A}{R^6}, \quad R \text{ large} \]
R decreases from $\infty \to <V>$ increases at first, $<T_{el}>$ decreases at first

Thus:

$<V>$ must go through a maximum somewhere between $R_e$ and infinity and $<T_{el}>$ must go through a minimum in this region.

For $R$ much less than $R_e$

$$U = E_{el} + V_{NN}$$

$$E_{el} = E_{UA} + aR^2 + bR^3 + cR^4 + \cdots$$

$$\hat{H} = \hat{H}_{mol} - \hat{H}_{UA}$$

$$U(R) \approx \frac{ZaZe^{2}}{R} + \frac{E_{UA} + aR^2}{R}, \quad R \text{ small}$$

$$\langle T_{el} \rangle = -U - R\frac{dU}{dR}, \quad \langle V \rangle = 2U + R\frac{dU}{dR}$$

$$\langle T_{el} \rangle \approx -E_{UA} - 3aR^2, \quad R \text{ small}$$

$$\langle V \rangle = \frac{ZaZe^{2}}{R} + 2E_{UA} + 4aR^2, \quad R \text{ small}$$

$R \to 0 \Rightarrow <V> \to \infty \quad$ because of the internuclear repulsion

Ali Ebrahimi
Variation of $\langle V \rangle$ and $\langle T_{el} \rangle$ of a diatomic molecule. The unit of energy is taken as the electronic kinetic energy of the separated atoms.

**Explanation:** The changes in $\langle T_{el} \rangle$ and $\langle V \rangle$ with $R$

Consider $H_2^+$:
electronic potential-energy function

$$V_{el} = -\frac{e^2}{r_a} - \frac{e^2}{r_b}$$

Potential energy along the internuclear axis for electronic motion in $H_2^+$ at a large internuclear separation. Atomic units are used.

We saw: overlapping of the 1s AOs increases the $\rho_{el}$ between the nuclei for GS. Fig. shows that the $V$ is relatively high in the region midway between the nuclei when $R$ is large. Thus $\langle V \rangle$ initially increases as $R$ decreases from infinity.
For a stationary state

\[ \langle p_x \rangle = 0 \quad \longrightarrow \quad (\Delta p_x)^2 = \langle p_x^2 \rangle \]

small \((\Delta x)^2\) \(\frac{\hbar^2}{4}\) \(\longrightarrow\) large \(\langle p_x^2 \rangle \) \(\longrightarrow\) a large value of \(\langle T_{el} \rangle\)

compact \(\Psi_{el} \rightarrow\) large \(\langle T_{el} \rangle\)

separated atoms : \(\Psi_{el}\) is compact
In the initial stages of molecule formation: \(\Psi_{el}\) is less compact
As \(R\) decreases from infinity \(T_{el}\) initially decreases

For large \(R\) : the region between the nuclei is classically forbidden, but it is accessible according to quantum mechanics (tunneling).

As \(R\) decreases further:
now the region between the nuclei is a region of low potential energy
charge buildup lowers \(V\)
intermediate values of \(R\) : wave function becomes more compact compared with large \(R\)
\(R \downarrow \Rightarrow \langle T_{el} \rangle \uparrow\)
\(\langle T_{el}^{\text{separated}} \rangle \langle T_{el} \rangle \Rightarrow\) molecular wave function at \(R_e\) is more compact than the separated-atoms wave functions.

it is the increase in \((T_{el})\), and not the nuclear repulsion, that causes the \(U(R)\) curve to turn up as \(R\) becomes less than \(R_e\).

\[ V \text{ along the internuclear axis for electronic motion in H}_2^+ \text{ at an intermediate internuclear distance.} \]
For very small $R$, the average potential energy goes to infinity, because of the internuclear repulsion. However, for $R = R_e$, Fig shows that $\langle V \rangle$ is still decreasing sharply with decreasing $R$, and the squeezing of the molecular wave function into a smaller region with the associated increase in $\langle T_\text{el} \rangle$ is more important than the internuclear repulsion in causing the initial repulsion between the atoms.

**THE HELLMANN-FEYNMAN THEOREM**

$H$: a time-independent Hamiltonian that involves parameters.

example:

$$H_{\text{el}} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_a \sum_i Z_a e_i^2 \frac{1}{r_{ia}} + \sum_i \sum_{j>i} e_i^2 \frac{1}{r_{ij}}$$

depends parametrically on the nuclear coordinates

one-dimensional harmonic-oscillator:

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

parameters: $k$, $m$

$\psi_n$ and $E_n$ are functions of the same parameters as $H$. 
How $E_n$ varies with each of the parameters?

$$\hat{H}\psi_n = E_n\psi_n$$

$$E_n = \int \psi_n^* \hat{H} \psi_n d\tau$$

Because of normalization

$$\frac{\partial E_n}{\partial \lambda} = \frac{\partial}{\partial \lambda} \left( \psi_n^* \hat{H} \psi_n \right) d\tau$$

depends parametrically on $\lambda$, since $\hat{H}$ and $\psi_n$ depend on $\lambda$.

All other parameters held constant

$$\frac{\partial E_n}{\partial \lambda} = \int \frac{\partial}{\partial \lambda} (\psi_n^* \hat{H} \psi_n) d\tau = \int \frac{\partial \psi_n^*}{\partial \lambda} \hat{H} \psi_n d\tau + \int \psi_n^* \frac{\partial}{\partial \lambda} (\hat{H} \psi_n) d\tau$$

$\hat{V}$ is just multiplication by $V$:

$$\frac{\partial}{\partial \lambda} (\hat{V} \psi_n) = \frac{\partial V}{\partial \lambda} \psi_n + V \frac{\partial \psi_n}{\partial \lambda}$$

Parameter $\lambda$ will occur in the kinetic-energy operator:

$$\frac{\partial}{\partial \lambda} (\hat{T} \psi_n) = \left( \frac{\partial}{\partial \lambda} \hat{T} \right) \psi_n + \hat{T} \left( \frac{\partial \psi_n}{\partial \lambda} \right)$$

$$\frac{\partial}{\partial \lambda} (\hat{H} \psi_n) = \left( \frac{\partial}{\partial \lambda} \hat{H} \right) \psi_n + \hat{H} \left( \frac{\partial \psi_n}{\partial \lambda} \right)$$
EXAMPLE

Apply the generalized Hellmann-Feynman theorem to the one-dimensional harmonic oscillator with $\lambda$ taken as the force constant.

\[
\frac{\partial E_n}{\partial \lambda} = \int \psi_n^* \frac{\partial \hat{H}}{\partial \lambda} \psi_n \, dx
\]

\[
\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} \lambda x^2 \quad \Rightarrow \quad \frac{\partial \hat{H}}{\partial \lambda} \frac{\partial \hat{H}}{\partial \lambda} = \frac{1}{2} x^2
\]

\[
E_n = (n + \frac{1}{2}) \hbar \nu = (n + \frac{1}{2}) \hbar k / (2m)^{1/2} \quad \Rightarrow \quad \frac{\partial E_n}{\partial \lambda} = \frac{1}{2} (v + \frac{1}{2}) \hbar k / (2m)^{1/2} / 2 \pi = \frac{1}{2} (v + \frac{1}{2}) \hbar \nu / k
\]

\[
\int_{-\infty}^{\infty} \psi_n^* x^2 \psi_n \, dx = (v + \frac{1}{2}) \hbar \nu / k
\]

Exercise:

For hydrogenlike atom, with $Z$ as the parameter, show:

\[
\int r^{-1} |\psi|^2 \, dr = \left\langle \frac{1}{r} \right\rangle = \frac{Z}{\pi^2} \left( \frac{1}{a_0} \right)
\]
A special case of the Hellmann-Feynman theorem

Where:

$$E_n^{(k)} = \frac{1}{k!} \left. \frac{d^k E_n}{d \lambda^k} \right|_{\lambda=0}, \quad k = 1, 2, \ldots$$

$$\hat{H} = \hat{H}^0 + \lambda \hat{H}'$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots + \lambda^k E_n^{(k)} + \cdots$$

The Hellmann-Feynman theorem with $E_n$ being the HF energy is obeyed by HF (as well as exact) wave functions.

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**THE ELECTROSTATIC THEOREM**

After Born-Oppenheimer approximation (for a fixed nuclear configuration)

$$\hat{H} \psi_{el} = (\hat{T}_{el} + \hat{V}) \psi_{el} = U \psi_{el}$$

$$\hat{V} = \hat{V}_{el} + \hat{V}_{NN}$$

$$\hat{T}_{el} = -\frac{k^2}{2m_e} \sum_{i} \left( \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right)$$

$$\hat{V}_{el} = -\sum_a \sum_i \frac{Z_a e^2}{\sqrt{(x_i - x_a)^2 + (y_i - y_a)^2 + (z_i - z_a)^2}}$$

$$+ \sum_i \sum_{j \neq i} \frac{e^2}{\sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}}$$

$$\hat{V}_{NN} = \sum_{\sigma \neq \sigma'} \sum_{a} \frac{Z_a Z_{\sigma'} e^2}{\sqrt{(x_a - x_{\sigma'})^2 + (y_a - y_{\sigma'})^2 + (z_a - z_{\sigma'})^2}}$$
\( \hat{H} \) depends on the nuclear coordinates as parameters.
\( x_\delta : x \) coordinate of nucleus \( \delta \).

\[
\frac{\partial E_n}{\partial \lambda} = \int \psi^*_n \frac{\partial \hat{H}}{\partial \lambda} \psi_n \, d\tau \\
\downarrow \\
\frac{\partial U}{\partial x_\delta} = \int \psi^*_\delta \frac{\partial \hat{H}}{\partial x_\delta} \psi_\delta \, d\tau_\delta
\]

GHF theorem

\( \vec{T}_\epsilon \) is independent of the nuclear Cartesian coordinates,

\[
\frac{\partial U}{\partial x_\delta} = \int \psi^*_\epsilon \frac{\partial V}{\partial x_\delta} \psi_\epsilon \, d\tau_\epsilon \\
\downarrow \\
\frac{\partial V}{\partial x_\delta} = \frac{\partial V_\epsilon}{\partial x_\delta} + \frac{\partial V_{NN}}{\partial x_\delta}
\]

\[
V_\delta = -\sum_a \sum_i \frac{Z_a e^2}{\left[(x_i - x_\delta)^2 + (y_i - y_\delta)^2 + (z_i - z_\delta)^2\right]^{1/2}} \\
+ \sum_i \sum_j \frac{e^2}{\left[(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2\right]^{1/2}}
\]

\[
\frac{\partial V_\epsilon}{\partial x_\delta} = -\sum_i \frac{Z_\epsilon (x_i - x_\delta)e^2}{r_\delta^3}
\]

\[
V_{NN} = \sum_{\sigma \neq \delta} \sum_i \frac{Z_\sigma Z_\epsilon e^2}{\left[(x_i - x_\delta)^2 + (y_i - y_\delta)^2 + (z_i - z_\delta)^2\right]^{1/2}}
\]

\[
\frac{\partial V_{NN}}{\partial x_\delta} = \frac{\partial}{\partial x_\delta} \sum_{\sigma \neq \delta} \frac{Z_\sigma Z_\epsilon e^2}{\left[(x_\sigma - x_\delta)^2 + (y_\sigma - y_\delta)^2 + (z_\sigma - z_\delta)^2\right]^{1/2}} = \sum_{\sigma \neq \delta} \frac{Z_\sigma Z_\epsilon e^2 (x_\sigma - x_\delta)}{R_{\sigma\delta}^3}
\]
\[ \frac{\partial U}{\partial x_\delta} = \int \psi_{\text{el}}^* \frac{\partial V}{\partial x_\delta} \psi_{\text{el}} d\tau_{\text{el}} \]

\[ \frac{\partial V_{\text{el}}}{\partial x_\delta} = -\sum_i \frac{Z_i(x_i - x_\delta)e^2}{r_i^3} \]

\[ \frac{\partial V_{\text{NN}}}{\partial x_\delta} = \sum_{\alpha \neq \delta} Z_\alpha Z_\delta e^2 \frac{x_\alpha - x_\delta}{R_{\alpha \delta}^3} \]

\[ \frac{\partial U}{\partial x_\delta} = -Z_\delta e^2 \left\{ \psi_{\text{el}}^* \sum_i \frac{x_i - x_\delta}{r_i^3} d\tau_{\text{el}} + \sum_{\alpha \neq \delta} Z_\alpha Z_\delta e^2 \frac{x_\alpha - x_\delta}{R_{\alpha \delta}^3} \right\} \]

\[ \int \psi_{\text{el}}^* \sum_i B(x_i) \phi \ d\tau = \int \rho(\tau) B(\tau) \ d\tau \]

\[ B(x_i) = \frac{(x_i - x_\delta)}{r_i} \]

\[ \frac{\partial U}{\partial x_\delta} = -Z_\delta e^2 \left\{ \int \int \rho(x, y, z) \frac{r_\delta}{r_\delta^3} dx \ dy \ dz + \sum_{\alpha \neq \delta} Z_\alpha Z_\delta e^2 \frac{r_\delta}{R_{\alpha \delta}^3} \right\} \]

\[ r_\delta = [(x - x_\delta)^2 + (y - y_\delta)^2 + (z - z_\delta)^2]^{1/2} \]

\[ r_\delta = [(x - x_\delta)^2 + (y - y_\delta)^2 + (z - z_\delta)^2]^{1/2} \]

\[ \frac{1}{2} \sum_a \frac{1}{m_a} \nabla_a^2 + U \right) \psi_{\text{el}} = E \psi_{\text{el}} \]

- \[ \frac{\partial U}{\partial x_\delta} \] can thus be viewed as the x component of the effective force on nucleus \( \delta \) due to the other nuclei and the electrons.

\[ F_\delta = - \frac{i}{\partial \psi_{\text{el}}}{\partial x_\delta} - \frac{j}{\partial \psi_{\text{el}}}{\partial y_\delta} - \frac{k}{\partial \psi_{\text{el}}}{\partial z_\delta} \]

\[ F_\delta = -Z_\delta e^2 \left\{ \int \int \rho(x, y, z) \frac{r_\delta}{r_\delta^3} dx \ dy \ dz + e^2 \sum_{\alpha \neq \delta} Z_\alpha Z_\delta \frac{R_{\alpha \delta}}{R_{\alpha \delta}^3} \right\} \]

\[ r_\delta \] is the vector from point \((x, y, z)\) to nucleus \( \delta \)

\[ r_\delta = i(x_\delta - x) + j(y_\delta - y) + k(z_\delta - z) \]

\[ R_{\alpha \delta} \] is the vector from nucleus \( \alpha \) to nucleus \( \delta \)

\[ R_{\alpha \delta} = i(x_\delta - x_\alpha) + j(y_\delta - y_\alpha) + k(z_\delta - z_\alpha) \]
simple physical interpretation:
imagine the electrons smeared out into a charge distribution whose
density is $-e \rho(x, y, z)$.

The force on nucleus $\delta$ exerted by the infinitesimal element of electronic charge
$-e \rho \, dx \, dy \, dz$:

$$- \frac{Z_{\delta} e^2}{r_{\delta}} \rho \, dx \, dy \, dz$$

$\rho = \rho(x, y, z; x_\alpha, y_\alpha, z_\alpha, x_\beta, \ldots)$

nuclear configuration

**Hellmann-Feynman electrostatic theorem**
The effective force acting on a nucleus in a molecule can be calculated by
simple electrostatics as the sum of the Coulombic forces exerted by the
other nuclei and by a hypothetical electron cloud whose charge density $-e \rho(x, y, z)$ is found by solving the electronic Schrodinger equation.

electrostatic theorem follows from the Born-Oppenheimer approximation.

---

electrostatic theorem and chemical bonding in diatomic molecules

Coordinate system for a diatomic molecule.
The origin is at O.

By symmetry, $F_{x,a} = F_{x,b} = F_{y,a} = F_{y,b} = 0$

$z$ force component on nucleus $a$:

$$F_{z,a} = -Z_{\delta} e^2 \iint \rho \, \frac{z_a - z}{r_a^3} \, dx \, dy \, dz - \frac{Z_{\delta} Z_{\beta} e^2}{R^3}$$
z component of effective force on nucleus a:

\[
F_{z,a} = -Z_a e^2 \int \int \int \rho \frac{z_a - z}{r_a^3} \, dx \, dy \, dz - \frac{Z_a Z_a e^2}{R^2}
\]

\[
r_a \cos \theta_a = -z_a + z
\]

\[
F_{z,a} = Z_a e^2 \int \int \int \rho \frac{\cos \theta_a}{r_a^2} \, dx \, dy \, dz - \frac{Z_a Z_a e^2}{R^2}
\]

Similarly:

\[
F_{z,b} = -Z_b e^2 \int \int \int \rho \frac{\cos \theta_b}{r_b^2} \, dx \, dy \, dz + \frac{Z_b Z_b e^2}{R^2}
\]

\[
F_{z,a} = -\frac{\partial U}{\partial z_a}
\]

\[
F_{z,a} = -\frac{dU(R)}{dR} \frac{\partial R}{\partial z_a}
\]

\[
R = \left( \left( x_a - x_b \right)^2 + \left( y_a - y_b \right)^2 + \left( z_a - z_b \right)^2 \right)^{1/2}
\]

\[
\frac{\partial R}{\partial x_a} = \frac{x_a - x_b}{R}, \quad \frac{\partial R}{\partial x_b} = \frac{x_b - x_a}{R}
\]

\[
F_{z,a} = -\frac{dU(R)}{dR} \frac{\partial R}{\partial z_a} = -\frac{dU}{dR} \frac{z_a - z_b}{R} = \frac{dU}{dR} \frac{\partial R}{\partial z_b} = -F_{z,b}
\]

equal in magnitude and opposite in direction

Ali Ebrahimi
The z component of the effective force on \(a\) caused by the element of electronic charge in the region about \((x, y, z)\)

\[ F_{z,a} = Z_a e^2 \int \int \rho \frac{\cos \theta_a}{r_a^2} \, dx \, dy \, dz - \frac{Z_a Z_e e^2}{R^2} \]

The z component of the effective force on \(b\) caused by the element of e charge in the region about \((x, y, z)\)

\[ F_{z,b} = -Z_b e^2 \int \int \rho \frac{\cos \theta_b}{r_b^2} \, dx \, dy \, dz + \frac{Z_b Z_e e^2}{R^2} \]

+ : force in the +z direction,

- \(F_a > F_b\) the element of e charge tends to draw \(a\) toward \(b\)

binding electronic charge locate in the region where:

\[ e^2 Z_a \rho \frac{\cos \theta_a}{r_a^2} \, dx \, dy \, dz > -e^2 Z_b \rho \frac{\cos \theta_b}{r_b^2} \, dx \, dy \, dz \]

\[ \rho \text{ is nonnegative,} \]

\[ A = \frac{Z_a \cos \theta_a}{r_a^2} + \frac{Z_b \cos \theta_b}{r_b^2} > 0 \]

- \(F_b > F_a\), the electronic charge element tends to draw \(b\) away from \(a\).

- \(A < 0\) : the antibinding region of space

- \(A = 0\) : The surfaces divide space into the binding and antibinding regions (was proposed by Berlin).
Cross section of binding and antibinding regions in a homonuclear diatomic molecule. To obtain the three-dimensional regions, rotate the figure about the internuclear axis.

Charge in this region tends to draw the nuclei together.

Charge in this region exerts a greater attraction on \( a \); tends to pull the nuclei apart.

Binding and antibinding regions for a heteronuclear diatomic molecule with \( Z_b > Z_a \).
Bader, Henneker, and Cade ...

**Hellmann-Feynman viewpoint**: chemical bonding is solely considered in terms of potential energy (imagining the electrons to be smeared out into a continuous charge distribution; no reference to electronic kinetic energy)

**Virial-theorem viewpoint**: involved both potential and kinetic energy.