Theorem of Mol QM

Chem 2430

Heterونuclear diatomic molecules

$CO \quad 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2$

Note $1\pi_x = c_1 2p_{Cx} + c_2 2p_{Ox}$

$|c_2| > |c_1|$ (based on electronegativities)

Due to orthogonality this implies $|c_2| < |c_1|$ for the $2\pi^*$ orbital.

HF $\quad 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4$

1σ essentially 100% F_{1s}

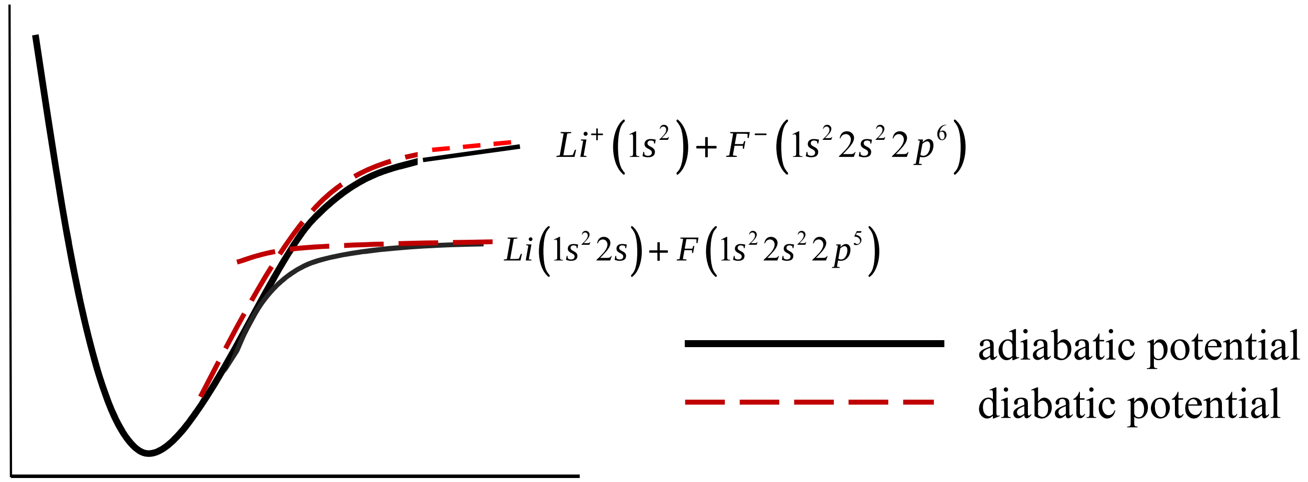
2σ mostly F_{2s} , small contribution H_{1s}

3σ strong admixture of H_{1s} , F_{2s} , F_{2pz}

1π essentially 100% F_{px} , F_{py}

LiF $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4$

largely Li$^+$ + F$^-$ in character at R$_e$



$IP \quad Li = 5.4\ \text{eV}$

$EA \quad F = 3.4\ \text{eV}$

So the ionic dissociation limit is 2eV above the covalent dissociation limit

The probability of finding an electron near a point (x, y, z) is

$$n\sum_{m_i}\int |\psi(x, y, z, x_2, y_2, z_2, \ldots, x_n, y_n, z_n)|^2 \, dx_2 \ldots dx_n$$

So for H_2 $\rho = 2\left|\sigma_g(r)\right|^2$

Suppose we were considering He_2

$$\rho = 2\left|1\sigma_g\right|^2 + 2\left|1\sigma_u\right|^2$$

For a single determinant wave function $\rho(x, y, z) = \sum_j n_j \left|\phi_j\right|^2$

n_j is the occupation number (1 or 2)

Consider an operator $B(r_i)$, where r_i denotes the coordinates of an electron

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

Dipole moments

For a set of point charges $\vec{\mu} = \sum Q_i \vec{r}_i,$

$\vec{r_i}$ is a vector from the origin to point charge *i*

For a continuous charge distribution

$\vec{\mu} = \int \rho_Q \left(x, y, z\right) \vec{r} dxdydz$ where ρ_Q is the charge distribution

$\boldsymbol{E} = {}^{\boldsymbol{F}}\!/_{Q}$ the electric field that a force exerts on a charge Q

Assume the applied field is in the z direction

$$\boldsymbol{E} = \varepsilon_z \boldsymbol{k}$$

$$dV/dz = -F_z = -Q\varepsilon_z, \quad V = -Q\varepsilon_z z$$

For multiple point charges $V = -\varepsilon_z \sum Q_i z_i$

In general $V = -\boldsymbol{E} \cdot \boldsymbol{\mu}$

In a QM treatment $\hat{H}' = -\boldsymbol{E} \cdot \hat{\boldsymbol{\mu}}$

$$E^{(1)} = -\boldsymbol{E} \bullet \int \psi^{(0)*} \hat{\boldsymbol{\mu}} \psi^{(0)} d\tau$$

$$\boldsymbol{\mu} = \int \psi^{(0)*} \hat{\boldsymbol{\mu}} \psi^{(0)} d\tau$$ permanent electric dipole moment

If a molecule has a center of symmetry $\boldsymbol{\mu} = 0$
We need to include the nuclear charges.

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

$$\boldsymbol{\mu} = -e \int \left|\psi_{el}\right|^2 \sum_i \boldsymbol{r}_i d\tau_{el} + e \sum_\alpha Z_\alpha \boldsymbol{r}_\alpha$$

$$= -e \int \rho\left(x, y, z\right) \boldsymbol{r}\, dxdydz + e \sum_\alpha Z_\alpha \boldsymbol{r}_\alpha$$

The second term derives from the nuclei

Note, that for a charged system the dipole moment depends on the chosen origin. So specifying the dipole moment of a charged molecule is meaningless unless the origin is also specified.

Virial Theorem $\left\langle \sum_i q_i \frac{\partial V}{\partial q_i} \right\rangle = 2\langle T \rangle$ where q_i is the coordinate

If the potential is a homogenous function of degree *n*

Harmonic osc: n = 2
H atom: n =-1

$$2\langle T \rangle = n\langle V \rangle, \quad \langle T \rangle + \langle V \rangle = E$$

$$\langle V \rangle = \frac{2E}{n+2}, \qquad \langle T \rangle = \frac{nE}{n+2}$$

Atom: $2\langle T \rangle = -\langle V \rangle$

For diatomic molecules

$$\langle T_{el} \rangle = -U - R\frac{dU}{dR}$$

$$\langle V \rangle = 2U + R\frac{dU}{dR}$$

at R= infinity and R=R$_e$, $\frac{dU}{dR} = 0$

At long distance $U(R) \approx U(\infty) - \frac{A}{R^6}$

$$\langle V \rangle = \langle V \rangle_\infty + \frac{4A}{R^6}$$

$$\langle T_{el} \rangle = \langle T_{el} \rangle - \frac{5A}{R^6}$$

$\langle V \rangle$ has max between $R = \infty$ and R_e

$\langle T \rangle$ has minimum between R_e
and $R = \infty$

At short distances

$$\langle T_{el} \rangle = \langle T_{el} \rangle_0 - 3aR^2$$

$$\langle V \rangle = \frac{Z_a Z_b}{R} + \langle V_{el} \rangle_0 + 4aR^2$$

Generalized Hellmann-Feynman Theorem

$$\frac{\partial E}{\partial \lambda} = \left\langle \psi_n \left| \frac{\partial H}{\partial \lambda} \right| \psi_n \right\rangle$$

where λ refers to some parameter in $\hat{H}$

Holds if $H\psi_n = E_n\psi_n$

So holds for full CI in a basis set.

Also holds for the HF wavefunction.

$$\left(\hat{T}_{el} + \hat{V}_{el} + \hat{U}_{NN}\right)\psi_{el} = U\psi_{el}$$

$$\frac{\partial U}{\partial x_\delta} = \left\langle \psi_{el} \left| \frac{\partial V_{el}}{\partial x_\delta} + \frac{\partial V_{NN}}{\partial x_\delta} \right| \psi_{el} \right\rangle$$

where x_σ refers to *x* coordinates of nucleus δ

Can show $\frac{\partial U}{\partial x_\delta} = -Z_\delta \int \rho(x,y,z) \sum_i \frac{x - x_\delta}{r_i^3} dxdydz + \sum_{\alpha \neq \delta} Z_\alpha Z_\delta \frac{x_\alpha - x_\delta}{R_{\alpha\delta}^3}$

Include y_δ and z_δ contributions

$$\boldsymbol{F}_\delta = -Z_\delta \int \rho(x,y,z) \frac{\boldsymbol{r}_\delta}{r_\delta^3} dxdydz + \sum_{\alpha \neq \delta} Z_\alpha Z_\delta \frac{\boldsymbol{R}_{\alpha\delta}}{R_{\alpha\delta}^3}$$

Hellmann-Feynman electrostatic theorem

The force on a nucleus is a consequence of Coulomb interactions

Note that in these equations. e’, the magnitude of the charge of the electron has been set equal to 1.