

Group theory and molecular spectroscopy. I.

The Schrödinger equation and symmetries

$$\hat{H}\Psi(\mathbf{r}_1, \dots, \mathbf{r}_n) = E\Psi(\mathbf{r}_1, \dots, \mathbf{r}_n)$$

$\forall g \in G : [\hat{g}, \hat{H}] = 0 \Rightarrow$ eigenfunctions of \hat{H} transform according to IRs of G .

Molecular states

Born–Oppenheimer approximation (small parameter = $\sqrt{m_e/m_p}$):

$$\Psi = \Psi_{el}(\mathbf{r}_1^e, \dots, \mathbf{r}_l^e; \sigma_1^e, \dots, \sigma_l^e) \otimes \Psi_N(\mathbf{r}_1^N, \dots, \mathbf{r}_n^N; \sigma_1^N, \dots, \sigma_n^N)$$

$$\Psi_N = \Psi_{rv}(\mathbf{r}_1^N, \dots, \mathbf{r}_n^N) \otimes \Psi_{NS}(\sigma_1^N, \dots, \sigma_n^N)$$

$$\Psi_{rv} = \Psi_r \otimes \Psi_v, \quad E = E_{el} + E_v + E_r$$

Electronic energy in the BO approximation

Nuclei are considered as classical particles; for given $\mathbf{r}_1^N, \dots, \mathbf{r}_n^N$ the Schrödinger equation for electrons is solved; the absolute minimum E_{el} with respect to $\mathbf{r}_1^N, \dots, \mathbf{r}_n^N$ yields the equilibrium configuration of the molecule (up to the translation of all particles by the same $\delta\mathbf{r}$ and rotation of the molecule).

Molecular vibrations

n -atomic molecule:

- ▶ $3n$ translational degrees of freedom in total;
- ▶ 3 degrees of freedom (DoF) of the center of mass;
- ▶ 2 rotational DoF for $n = 2$ or a linear molecule with $n > 2$ (e.g., C_2H_2) or 3 rotational DoF for a non-linear molecule ($n > 2$);
- ▶ As the result: # of vibrational DoF $\mathcal{N}_v = 3n - 5$ or $3n - 6$

Electronic energy can be considered as the potential energy with resp. to the positions of nuclei. Potential minimum for the equilibrium configuration \Rightarrow harmonic potential with resp. to small deviations $\delta \mathbf{r}_j^N$ from the equilibrium.

Constraints:

1. $\sum_{j=1}^n \delta \mathbf{r}_j^N = 0$ excludes center-of-mass motion; this constraint makes it natural, to set the origin of the co-ordinate system at the molecule's center of mass.
2. $\delta \mathbf{r}_j^N [\mathbf{e}_\alpha \times \mathbf{r}_j^N] = 0$ for all $j = 1, \dots, n$ and $\alpha = x, y, z$ excludes rotational motion.

To a harmonic approximation (normal co-ordinates!)

$$E_v = \sum_{\ell=1}^{\mathcal{N}_v} \hbar \omega_\ell (v_\ell + \frac{1}{2}), \quad v_\ell = 0, 1, 2, \dots$$

Some frequencies ω_ℓ may be degenerate (depending on the symmetry of the molecule).

Rotational energy

We set the origin of the co-ordinate frame to the center of mass,

$$\sum_{j=1}^n m_j \mathbf{r}_j^N = 0.$$

Moment of inertia tensor:

$$\mathcal{J}_{\alpha\beta} = \sum_{j=1}^n m_j r_{j\alpha}^N r_{j\beta}^N, \quad \alpha, \beta = x, y, z.$$

This symmetric tensor can be diagonalized by an orthogonal transformation to main axes. Setting x, y, z along main axes:

$$\mathcal{J}_{\alpha\beta} = 2\tilde{B}_\alpha^{-1} \delta_{\alpha\beta}$$

Classical rotation energy: $E_r = \sum_{\alpha=x,y,z} \tilde{B}_\alpha J_\alpha^2$, where J_α is a projection of angular momentum \mathbf{J} of rotating nuclei to the axis α .

Hamiltonian of a quantum rigid rotor:

$$\hat{H}_r = \sum_{\alpha=x,y,z} B_\alpha \hat{J}_\alpha^2, \quad B_\alpha = \hbar^2 \tilde{B}_\alpha$$

Symmetric rigid rotor

$$B_x = B_y \equiv B_{\perp}, \quad B_z = B_{\parallel} \neq B_{\perp}$$

$$\hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 = \hat{\mathbf{J}}^2$$

$$\hat{H}_r = B_{\perp} \hat{\mathbf{J}}^2 + (B_{\parallel} - B_{\perp}) \hat{J}_z^2$$

Quantum numbers:

$$J = 0, 1, 2, \dots; \quad M = -J, -J + 1, \dots, 0, \dots, J - 1, J;$$

$$K = -J, -J + 1, \dots, 0, \dots, J - 1, J$$

Wave function (up to normalization) is a complex-conjugate Wigner D -function: $\Phi_{JMK}(\phi, \theta, \chi) = D_{MK}^{J*}(\phi, \theta, \chi) = e^{iM\phi} d_{MK}^J(\theta) e^{iK\chi}$

K is the projection of the rotational angular momentum to the molecular axis z ; M is the projection to the lab (non-moving) axis Z .

$$E_r = B_{\perp} J(J + 1) + (B_{\parallel} - B_{\perp}) K^2$$

Spherical rotor

$$B_x = B_y = B_z \equiv B$$

$$\hat{H}_r = B\hat{\mathbf{J}}^2, \quad E_r = BJ(J+1)$$

$$\Phi_{JMK}(\phi, \theta, \chi) = D_{MK}^{J*}(\phi, \theta, \chi) = e^{iM\phi} d_{MK}^J(\theta) e^{iK\chi}$$

Linear / diatomic molecules

Two rotational degrees of freedom \Rightarrow two quantum numbers

$$J = 0, 1, 2, \dots; \quad M = -J, -J+1, \dots, 0, \dots, J-1, J.$$

Wave function is given by a spherical harmonic $Y_{JM}(\theta, \phi)$,

$$E_r = BJ(J+1)$$

Asymmetric rotor

All three B_x , B_y , B_z are different.

We introduce

$$\hat{J}_{\pm} = \frac{1}{\sqrt{2}}(\hat{J}_x \pm i\hat{J}_y), \quad \hat{J}_- = \hat{J}_+^{\dagger}$$

$$\hat{\mathbf{J}}^2 = \hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+ + \hat{J}_z^2$$

$$\hat{H}_r = B_+\hat{\mathbf{J}}^2 + B_-(\hat{J}_+^2 + \hat{J}_-^2) + (B_z - B_+)\hat{J}_z^2,$$

$$B_{\pm} = \frac{1}{2}(B_x \pm B_y)$$

This Hamiltonian can be diagonalized numerically using

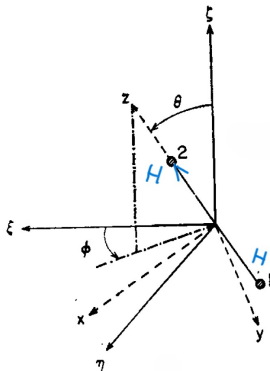
$$\hat{\mathbf{J}}^2\Phi_{JMK} = J(J+1)\Phi_{JMK}, \quad \hat{J}_z^2\Phi_{JMK} = K^2\Phi_{JMK},$$

$$\hat{J}_+^2\Phi_{JMK} = \frac{1}{2}\sqrt{[J(J+1)-K(K+1)][J(J+1)-(K+1)(K+2)]}\Phi_{JMK+2}$$

$$\hat{J}_-^2\Phi_{JMK} = \frac{1}{2}\sqrt{[J(J+1)-K(K-1)][J(J+1)-(K-1)(K-2)]}\Phi_{JMK-2}$$

Hydrogen molecule

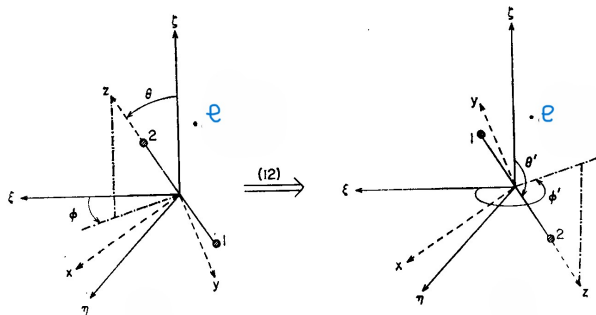
H_2 in rovibronic co-ordinates (centered at the center of masses)



R = distance between the two nuclei; (x,y,z) = co-ord. of electrons.

Symmetry operations: e , inversion E^* , permutation of two identical nuclei (12) , and $(12)^* \equiv (12)E^* = E^*(12)$.

Permutation (12)



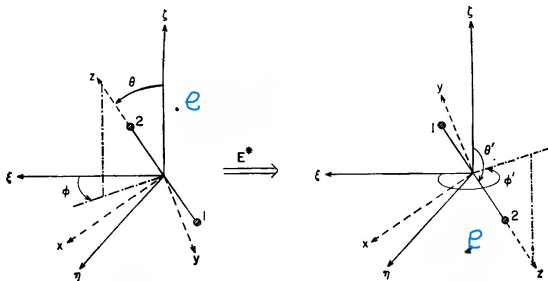
$$R' = R$$

$$\theta' = \pi - \theta, \quad \phi' = \phi + \pi$$

For electrons: $z' = -z$, $y' = -y$, $x' = x$;

since the co-ordinate system remains right-handed, only two co-ordinates change the sign.

Inversion E^*



$$R' = R$$

$$\theta' = \pi - \theta, \quad \phi' = \phi + \pi$$

For electrons: $z' = z$, $y' = y$, $x' = -x$;

the transformed co-ordinate system is the same as after (12), but electrons are inverted w.r.t. its origin \Rightarrow only one co-ordinate changes the sign.

Molecular term for a diatomic molecule

A molecule, unlike an atom, has no spherical symmetry, $[\hat{\mathbf{L}}^2, \hat{H}] \neq 0$.
Good quantum numbers: \mathbf{S}^2 , L_z , $L_z + S_z$, where $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ are electronic orbital momentum and spin, respectively.

$$^{2S+1}\Lambda$$

$2S + 1 =$ multiplicity,

$\Lambda = \Sigma, \Pi, \Delta, \dots$ corresponds to $|L_z| = 0, 1, 2, \dots$

Degeneracy is $2S+1$ for Σ states and $2(2S+1)$ for Π, Δ, Φ, \dots states.

If spin-orbit coupling is important:

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

$$\Omega = |L_z + S_z|$$

(2-fold degeneracy for $\Omega \neq 0$)

Homonuclear diatomic molecules

$$^{2S+1}\Lambda_{\Omega,g/u}^{\pm}$$

\pm : electronic wave function $\frac{\text{does no change}}{\text{changes}}$ its sign after E^* .

This notation is obsolete for Π, Δ, \dots states and applies for Σ^+ and Σ^- .

g = gerade, u = ungerade

$\left. \begin{matrix} g \\ u \end{matrix} \right\}$: electronic wave function $\frac{\text{does no change}}{\text{changes}}$ its sign after $(12)^*$.

H_2 molecule, as most of the diatomic molecules, has a fully symmetric electronic ground state $^1\Sigma_g^+$.

There are few exceptions, e.g., $\text{O}_2: ^3\Sigma_g^-$ and $\text{NO}: ^2\Pi$.

Ortho- and para-hydrogen

Spin of the proton: $i = 1/2$.

$I = 0$ state:

$$\langle \sigma_1, \sigma_2 | 0, 0 \rangle = \frac{1}{\sqrt{2}} \left(\langle \sigma_1 | \frac{1}{2}, +\frac{1}{2} \rangle \langle \sigma_2 | \frac{1}{2}, -\frac{1}{2} \rangle - \langle \sigma_1 | \frac{1}{2}, -\frac{1}{2} \rangle \langle \sigma_2 | \frac{1}{2}, +\frac{1}{2} \rangle \right)$$

$$\langle \sigma_1, \sigma_2 | 0, 0 \rangle = - \langle \sigma_2, \sigma_1 | 0, 0 \rangle$$

$I = 1$ state:

$$\langle \sigma_1, \sigma_2 | 1, 0 \rangle = \frac{1}{\sqrt{2}} \left(\langle \sigma_1 | \frac{1}{2}, +\frac{1}{2} \rangle \langle \sigma_2 | \frac{1}{2}, -\frac{1}{2} \rangle + \langle \sigma_1 | \frac{1}{2}, -\frac{1}{2} \rangle \langle \sigma_2 | \frac{1}{2}, +\frac{1}{2} \rangle \right)$$

$$\langle \sigma_1, \sigma_2 | 1, +1 \rangle = \langle \sigma_1 | \frac{1}{2}, +\frac{1}{2} \rangle \langle \sigma_2 | \frac{1}{2}, +\frac{1}{2} \rangle$$

$$\langle \sigma_1, \sigma_2 | 1, -1 \rangle = \langle \sigma_1 | \frac{1}{2}, -\frac{1}{2} \rangle \langle \sigma_2 | \frac{1}{2}, -\frac{1}{2} \rangle$$

$$\langle \sigma_1, \sigma_2 | 1, M_I \rangle = + \langle \sigma_2, \sigma_1 | 1, M_I \rangle$$

Fermi–Dirac statistics:

$$(12) |\Psi_{el}\rangle |\Psi_v\rangle |\Psi_r\rangle = \begin{cases} + |\Psi_{el}\rangle |\Psi_v\rangle |\Psi_r\rangle & , \quad I = 0 \\ - |\Psi_{el}\rangle |\Psi_v\rangle |\Psi_r\rangle & , \quad I = 1 \end{cases}$$

The electronic state $^1\Sigma_g^+$ is symmetric w.r.t. (12).

(12) changes only angular variables, but does not affect the vibrational DoF in H_2 , therefore $(12)|\Psi_\nu\rangle = +|\Psi_\nu\rangle$, regardless of the vibrational quantum number ν .

Due to the change $\theta' = \pi - \theta$, $\phi' = \phi + \pi$: $(12)|\Psi_r\rangle = (-1)^J |\Psi_r\rangle$.

J odd $\Leftrightarrow I = 1$ (ortho-hydrogen)

J even $\Leftrightarrow I = 0$ (para-hydrogen)

D_2 molecule ($i = 1$, Bose–Einstein statistics)

J odd $\Leftrightarrow I = 1$ (para- D_2)

J even $\Leftrightarrow I = 0, 2$ (ortho- D_2)