

MIT OpenCourseWare
<http://ocw.mit.edu>

5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

For information about citing these materials or our Terms of Use, visit: <http://ocw.mit.edu/terms>.

Lecture #8: The Born-Oppenheimer Approximation

For atoms we use SCF to define $1e^-$ orbitals. Get $V_i^{\text{eff}}(r)$ for each e^- in field of e^- 's in all other occupied orbitals.

$$\psi(\underline{r}) = |\phi_1(r_1) \dots \phi_N(r_N)| \quad \text{single antisymmetrized product function.}$$

This is a way of defining our zero-order complete basis set.

It is a bad approximation and accurate *ab initio* electronic wavefunctions are CI — linear combination of many configurations (product functions).

For molecules, we separate $\Psi(\underline{r}; R, \theta, \phi)$ into a product of electronic, vibrational, and rotational functions $\Phi_i(\underline{r}; R) \chi_{i, \nu, \Omega} |\Omega J M\rangle$.

This is the Born-Oppenheimer approximation. It is based on a good approximation (e^- move much faster than nuclei) and most molecular eigenstates can be well described by single electronic*vibrational*rotational product.

BUT WHAT DO WE HAVE TO SLIP UNDER THE RUG?

How to separate $\hat{H}(\underline{r}, R, \theta, \phi)$? some subtle stuff — return to this for polyatomic molecules

1. CLAMPED NUCLEI

$$T^N \rightarrow 0 \text{ get electronic } \Phi_i(\underline{r}; R) \text{ and nuclear } V_i(R) \text{ by neglecting } \langle \Phi_i | \hat{\nabla}^2 | \Phi_j \rangle \text{ and } \langle \Phi_i | \hat{\nabla} | \Phi_j \rangle \hat{\nabla} \chi(R).$$

2. For the i -th electronic state, $\hat{H}^{\text{ROT-VIB}}(R, \theta, \phi)$ separated into $\hat{H}^{\text{ROT}}(\theta, \phi) + \hat{H}^{\text{VIB}}(R)$

define $|\Omega J M\rangle$ basis set
 neglect part of \mathbf{H}^{ROT}
 Define $V_{i, \nu, \Omega}(R) = V_i(R) + B_i(R)[J(J+1) - \Omega^2]$ effective potential
 Define $\chi_{i, \nu, \Omega}(R)$ vibrational basis set.

3. EXACT ψ — use BO ψ^0 to go beyond BO approximation, then put the neglected terms back into

\hat{H}
 spectroscopic perturbations
 adiabatic vs. diabatic limits (neglect of either ∇^2 or electrostatic terms)

Potential Energy Surfaces are the central organizing concept of molecular spectroscopy.

Recipe:

1. write exact \hat{H}
2. neglect inconvenient terms
3. solve the simplified equation to define a complete basis set
4. put the neglected terms back in.

$$\hat{H} = \hat{T}^e + \hat{T}^N + V^{eN} + V^{NN} + V^{ee}$$

$$\hat{T}^e = \sum_i \frac{p_i^2}{2m_e} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2$$

Defined with respect to center of mass. See [Bunker, *J. Mol. Spect.* **28**, 422 (1968)] for neglected e^- induced center of mass wobble.

$$\hat{T}^N = \frac{\hat{p}_A^2}{2m_A} + \frac{\hat{p}_B^2}{2m_B} \rightarrow \hat{T}^N(R, \theta, \phi) = \hat{T}^N(R) + \hat{H}^{\text{ROT}}(\hat{R}; \theta, \phi)$$

internuclear distance

orientation of \hat{R} with respect to lab XYZ

radial only KE $\hat{T}^N(R) = -\frac{\hbar^2}{2\mu R^2} \left[\frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) \right]$

$$\hat{H}^{\text{ROT}}(R, \theta, \phi) = -\frac{\hbar^2}{2\mu R^2} (\hat{R}^2)$$

rotational constant $hcB(R)$

nuclear angular momentum

$$\hat{R} \equiv \hat{J} - \hat{L} - \hat{S} \quad \mu = \frac{m_A m_B}{m_A + m_B}$$

$$V^{eN} = -\sum_i \left[\frac{Z_A e^2}{|r_i - R_A|} + \frac{Z_B e^2}{|r_i - R_B|} \right]$$

$$V^{NN} = +\frac{Z_A Z_B e^2}{R}$$

$$V^{ee} = +\sum_{i>j} e^2/r_{ij} \quad \text{spoils } 1e^- \text{ orbital approximation} \rightarrow \text{SCF}$$

Two coordinate systems

LAB XYZ } both have origin at center of mass (definition of body frame becomes more
BODY xyz }

complex for polyatomic molecules)

related by 3 Euler angles (need only 2 angles to locate internuclear axis, 3rd angle chosen implicitly = phase convention)

Can we separate $\hat{H} = \hat{H}^{\text{el}} + \hat{H}^{\text{VIB}} + \hat{H}^{\text{ROT}}$?

if we could, then $E_{\text{evr}} = T_i + G_i(v) + F_{iv}(J)$

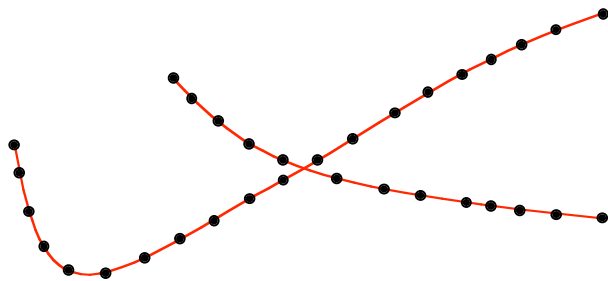
$$\Psi_{\text{evr}} = |\phi_i\rangle |\chi_v^i\rangle |\Omega JM\rangle$$

NOT quite.

e^- move fast, nuclei slow. Take this to extreme limit and pretend nuclei can be held fixed.

CLAMPED NUCLEI $T^N \rightarrow 0$

solve clamped nuclei electronic Schrödinger Equation at grid of fixed $R : R_1, R_2, \dots R_n$



manifold of eigenstates, computed at grid of R_n points

$$\hat{\mathbf{H}}(\underline{r}; \underbrace{R_n}_{\text{grid point}}) \Phi_i(\underline{r}; R_n) = E_i(R_n) \Phi_i(\underline{r}; R_n) \quad R_n \text{ fixed}$$

This defines $E_i(R)$ which we call the potential energy function for the i -th electronic state $V_i(R)$.

This also defines $\Phi_i(\underline{r}; R)$ a complete set of electronic wavefunctions which depend parametrically on R .

Next: use $E_i(R)$ and $\Phi_i(\underline{r}; R)$ to define a (non-rotating) ($T_{\theta, \phi}^N \rightarrow 0$) nuclear motion Schrödinger Equation.

$$\Psi_{i,v}^{\text{BO}}(\underline{r}; \mathbf{R}) \equiv \Phi_i(\underline{r}; \mathbf{R}) \chi_{i,v}(\mathbf{R}) \quad (\text{no } \theta, \phi \text{ dependence})$$

plug into full Schrödinger Equation, left multiply by $\Phi_i^*(\underline{r}; \mathbf{R})$ and integrate over all \underline{r} : denoted as $\langle \rangle_r$.

$$\begin{aligned} \hat{\mathbf{H}}\Psi^{\text{BO}} &= E\Psi^{\text{BO}} \\ \langle \Phi_i | \hat{\mathbf{H}} | \Phi_i \rangle_r \chi_{i,v} &= E \langle \Phi_i | \Phi_i \rangle_r \chi_{i,v} \\ \uparrow & \quad \text{independent of } r \quad \quad \quad = 1 \quad \quad \quad \text{independent of } r \\ \hat{\mathbf{T}}^N(\mathbf{R}) + E_i(\mathbf{R}) & \quad \quad \quad \uparrow \text{ came from } T^e + V^{eN} + V^{NN} + V^{ee} \text{ only} \\ \langle \Phi_i | \hat{\mathbf{T}}^N | \Phi_i \rangle_r \chi_{i,v} + \underbrace{E_i(\mathbf{R})}_{V_i(\mathbf{R})} \chi_{i,v} &= E \chi_{i,v}(\mathbf{R}) \\ \left(\frac{-\hbar^2}{2\mu} \nabla_{\mathbf{R}}^2 \right) \chi_{i,v} + V_i(\mathbf{R}) \chi_{i,v} &= E \chi_{i,v}(\mathbf{R}) \\ \text{eigenvalue equation, } \chi_{i,v}(\mathbf{R}) &\leftrightarrow E_{i,v} \end{aligned}$$

Chain rule for ∇^2

$$\nabla^2(AB) = \nabla[(\nabla A)B + A\nabla B] = (\nabla^2 A)B + (\nabla A)(\nabla B) + (\nabla A)(\nabla B) + A(\nabla^2 B)$$

Thus

$$\begin{aligned} \langle \Phi_i | \hat{T}^N | \Phi_i \rangle_r \chi_{i,v} &= \langle \phi_i | \hat{T}^N | \phi_i \rangle_r \chi_{i,r} + 2 \left(-\frac{\hbar^2}{2\mu} \right) \langle \phi_i | (\nabla_R \phi_i)_r \rangle \nabla_R \chi_{i,v} \\ &\quad \underbrace{\hspace{15em}}_{\text{do we expect } \phi_i \text{ to depend on } R?} \\ &+ \underbrace{\langle \phi_i | \phi_i \rangle_r}_{=1} \hat{T}^N \chi_{i,v} \\ &\quad \underbrace{\hspace{10em}}_{\text{keep this, neglect the other two terms}} \end{aligned}$$

We are left with $\underbrace{\hat{H}}^{\text{VIBR}} [\hat{T}^N(\mathbf{R}) + V_i(\mathbf{R})]\chi_{i,v} = E_{i,v}\chi_{i,v}(\mathbf{R})$ nuclear Schrödinger Equation

So are we done yet? Nope. We must reconsider neglected terms from T^N including rotation.

The nuclear motion $\hat{H}(\mathbf{R}, \theta, \phi)$ is **not quite** separable into $\hat{h}_1(\mathbf{R}) + \hat{h}_2(\theta, \phi)$ (worse for polyatomics)

Another trick is needed to separate out θ, ϕ degrees of freedom.

$$\hat{H}_i(\mathbf{R}, \theta, \phi) = T^N(\mathbf{R}) + \underbrace{\frac{\hbar^2}{2\mu R^2}}_{\substack{\text{rotational constant} \\ \text{operator - depends on } R}} \left[\hbar^{-2} \hat{\mathbf{R}}^2 \right] + V_i(\mathbf{R})$$

notation is tricky here

nuclear rotation angular momentum — depends on θ, ϕ

BAD NEWS
 $R \leftrightarrow \theta, \phi$ coupling, therefore can't separate!

The trick is to use a standard set of angular momentum basis functions [analogous to the $Y_l^m(\theta, \phi)$ of the central force problem], then define what we have to temporarily throw away so that we can integrate over θ, ϕ to get a new and correct rotating molecular Schrödinger Equation.

Define $|\Omega JM\rangle$ basis functions. Eigenfunctions of $\mathbf{J}_z, \mathbf{J}^2, \mathbf{J}_z$

They are $f(\theta, \phi)$ and describe probability of finding internuclear axis (BODY z axis) pointing in θ, ϕ direction (with respect to lab) given that the magnitude of the angular momentum is $[J(J+1)]^{1/2}$ and that the projection of \vec{J} on Z is M and on z is Ω
i.e.

$$\begin{aligned} \text{DIRECTION COSINES} \quad \cos(\vec{J}, Z) &= \frac{M}{[J(J+1)]^{1/2}} & J^2 |\Omega JM\rangle &= \hbar^2 J(J+1) |\Omega JM\rangle \\ \cos(\vec{J}, z) &= \frac{\Omega}{[J(J+1)]^{1/2}} & J_z |\Omega JM\rangle &= \hbar M |\Omega JM\rangle \\ & & J_z |\Omega JM\rangle &= \hbar \Omega |\Omega JM\rangle \end{aligned}$$

$$\hat{J} = \hat{R} + \hat{L} + \hat{S}$$

Total angular momentum is conserved, so it must be true that $[\hat{H}, \hat{J}^2] = 0$.

J is a rigorously good quantum number. What about Ω and M? Why?

\therefore better to use \hat{J}^2 than \hat{R}^2 , but J does not appear in $\hat{H}(\mathbf{R}, \theta, \phi)$.

We are going to temporarily throw away some stuff. (Some clever algebra needed to reduce \hat{R}^2 to this simple form.)

$$\begin{aligned} \hat{R} &= \hat{J} - \hat{L} - \hat{S} \\ \hat{R}^2 &= (J^2 - J_z^2) + [(S^2 - S_z^2) + (L^2 - L_z^2) \\ &\quad - 2(J_x L_x + J_y L_y) \quad \text{L-uncoupling} \\ &\quad - 2(J_x S_x + J_y S_y) \quad \text{S-uncoupling} \\ &\quad + 2(L_x S_x + L_y S_y)] \end{aligned}$$

temporarily get rid of all stuff in []

$$(J^2 - J_z^2) |\Omega JM\rangle = \hbar^2 [J(J+1) - \Omega^2] |\Omega JM\rangle$$

Now we can get rid of θ, ϕ part of $\hat{H}_i(\mathbf{R}, \theta, \phi)$

Express unknown $\chi_{i,v}(\mathbf{R}, \theta, \phi)$ as product of radial and angular factors,

$$\chi_{i,v,J,\Omega,M}(\mathbf{R}) = \langle \mathbf{R} | i v J \Omega M \rangle \text{ and } \left| \underbrace{\Omega JM}_{\theta, \phi} \right\rangle = \langle \theta, \phi | \Omega JM \rangle$$

$\chi_{i,v}(\mathbf{R}, \theta, \phi) \equiv \sum_{J\Omega M} \chi_{i,v,J,\Omega,M}(\mathbf{R}) |\Omega JM\rangle$ (usual schizophrenic approach: vibration as wavefunction, rotation as state vector).

left multiply Schrödinger Equation expressed in terms of $\hat{H}(\mathbf{R}, \theta, \phi)$ by $\langle \Omega JM |$ and integrate over θ, ϕ .

$$\left\langle \Omega J M \left| \hat{H}(\mathbf{R}, \theta, \phi) \right| \sum_{\Omega' J' M'} \chi_{iv\Omega' J' M'}(\mathbf{R}) \right| \Omega' J' M' \rangle_{\theta\phi} = \left\langle \Omega J M \left| E_{ivJ\Omega} \right| \sum_{\Omega' J' M'} \chi_{iv\Omega' J' M'} \right| \Omega' J' M' \rangle_{\theta\phi}$$

$$\text{LHS} = \left\{ T^N(\mathbf{R}) + V_i(\mathbf{R}) + B(\mathbf{R})[J(J+1) - \Omega^2] \right\} \underbrace{\left\langle \Omega J M \left| \sum_{\Omega' J' M'} \right| \Omega' J' M' \right\rangle_{\phi\theta}}_{\text{orthonormality}} \chi_{iv\Omega J M}$$

(All of this comes out of the θ, ϕ integral because the terms are independent of θ, ϕ or because we used $|\Omega J M\rangle$ basis functions.)

$$+ \left\langle \Omega J M \left[\text{neglected stuff from } \hat{R}^2 \right] \right| \sum_{\Omega' J' M'} \left| \Omega' J' M' \right\rangle \chi_{iv\Omega' J' M'}$$

some non-zero $\Delta\Omega = \pm 1$ matrix elements.
Neglect for now. Perturbations and L,S
uncoupling later!

Simplifies to:

$$\text{LHS} \cong \left\{ T^N(\mathbf{R}) + \underbrace{V_i(\mathbf{R}) + B(\mathbf{R})[J(J+1) - \Omega^2]}_{\substack{\text{call this } V_{i,J\Omega}(\mathbf{R}) \\ \text{"effective potential curve"}}} \right\} \chi_{iv\Omega J M}$$

$$\text{RHS} = E_{ivJ\Omega} \chi_{iv\Omega J M}(\mathbf{R})$$

None of the operators on the LHS depend on M or J_z , drop this index. Now at last we have a simple R-equation.

$$\left[\hat{T}^N(\mathbf{R}) + V_{i,J\Omega}(\mathbf{R}) \right] \chi_{ivJ\Omega} = E_{ivJ\Omega} \chi_{ivJ\Omega}$$

different set of vibrational χ 's for each J, Ω (we can avoid this by Van Vleck transformation, later)

So we are almost done. We have defined a complete basis set.

$$\psi_{ivJ\Omega}^{\text{BO}}(r; \mathbf{R}, \theta, \phi) = \Phi_i(r; \mathbf{R}) \chi_{ivJ\Omega}(\mathbf{R}) \langle \theta\phi | \Omega J M \rangle$$

* $\Phi_i(r; \mathbf{R})$ is an eigenfunction of $\hat{\mathbf{H}} - \hat{\mathbf{T}}^N(\mathbf{R}, q, f)$ ($\hat{\mathbf{T}}^N$ is removed because we clamped the nuclei)

* $|\Omega J M\rangle$ is eigenfunction of J^2, J_z, J_z and approximate eigenfunction of $\hat{\mathbf{T}}^N(\mathbf{R}, \theta, \phi) - \hat{\mathbf{T}}^N(\mathbf{R})$

$$= \frac{\hbar^2}{2\mu R^2} \hat{\mathbf{R}}^2 = B(\mathbf{R}) [\hat{J} - \hat{L} - \hat{S}]^2 \approx B(\mathbf{R}) [\hat{J}^2 - \hat{J}_z^2]$$

* $\chi_{ivJ\Omega}(\mathbf{R})$ is eigenfunction of $\hat{\mathbf{T}}^N(\mathbf{R}) + V_{iJ\Omega}(\mathbf{R})$

All we need now is the exact ψ

$$\psi_J^{\text{exact}} = \sum_{i, v, \Omega} \psi_{ivJ\Omega}^{\text{Born-Oppenheimer}} c_{ivJ\Omega}$$

mixing coefficient

The Born-Oppenheimer approximation is a good approximation when only one term in summation is important.

IN THIS SPECIAL CASE

$$E_{cvJ} = T_i + G_i(v) + F_{i,v}(J)$$

and it is straightforward to go in either direction

$$E_{cvJ} \leftrightarrow V_{ij}(\mathbf{R})$$

Sometimes a few mixing coefficients are important — must “go beyond the Born-Oppenheimer approximation” — “PERTURBATIONS” (local vs. global)

Perturbation Theory

The “nominal” k, v, J state is denoted by putting it between ‘ ’.

$$\psi_{'kvJ'}^{\text{EXACT}} = \psi_{kvJ}^{\text{Born-Oppenheimer}} + \sum_{i, v'} \frac{H_{iv'J; kvJ}}{E_{kvJ}^o - E_{iv'J}^o} \psi_{iv'J}^{\text{Born-Oppenheimer}}$$

1st order corrections to ψ . If one or more of these correction terms is too large, must diagonalize a matrix.

What terms in $\hat{\mathbf{H}}$ cause trouble?

$V^{ee} = e^2/r_{ij}$ explicitly included in definition of ψ^{oBO} which is also called the “adiabatic” wavefunction. This keeps potential curves for states of same symmetry from crossing. Non-crossing rule.

$T^N(\mathbf{R})$ ignored effect on $\Phi_i(\mathbf{r};\mathbf{R})$

\mathbf{H}^{ROT} ignored effects of stuff in []. These effects can be turned off by going to $J = 0$.

Two convenient limits

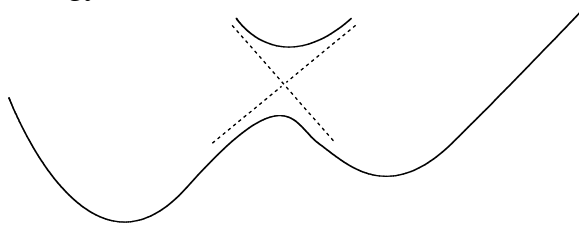
1. Adiabatic or Born-Oppenheimer

define Φ_i^{ad} electronic basis functions by exactly diagonalizing $\hat{\mathbf{H}} - T^N(\mathbf{R})$

treat $T^N(\mathbf{R})$ as a perturbation

e.g. $\left\langle \psi_i^{BO} \left| \frac{\partial}{\partial \mathbf{R}} \right| \psi_j^{BO} \right\rangle \neq 0$ because ψ 's are \mathbf{R} -dependent — especially rapid change near avoided crossings $\mathbf{R} \approx \mathbf{R}_c$

get non-crossing potential energy curves



2. DIABATIC Φ_i^d

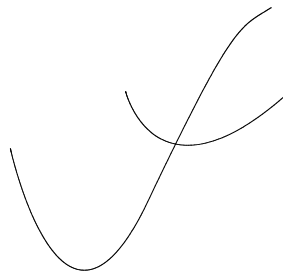
exclude some undefinable part of V^{ee} in order to define “single configuration” electronic basis states.

Treat $\hat{\mathbf{H}}^{el}$ (that undefinable part of V^{ee}) as a perturbation

e.g. $\left\langle \Phi_i^d \left| \frac{\partial}{\partial \mathbf{R}} \right| \Phi_j^d \right\rangle = 0$ (we refuse to let Φ^d depend on \mathbf{R})

because $\frac{\partial}{\partial \mathbf{R}} \Phi_j^d \equiv 0$ but $\left\langle \Phi_i^d \left| \hat{\mathbf{H}}^{el} \right| \Phi_j^d \right\rangle \neq 0$

get crossing curves



Two limiting cases

Weakly avoided crossing — diabatic basis is preferable because $\left\langle i \left| \frac{\partial}{\partial \mathbf{R}} \right| j \right\rangle$ is very large for \mathbf{R} near crossing.

Strongly avoided crossing — adiabatic basis is preferable because $\left\langle i \left| \hat{\mathbf{H}}^{\text{el}} \right| j \right\rangle$ would be large relative to all vibrational level spacings.