Transforming the Vibrational Hamiltonian of a Polyatomic Molecule Using Van Vleck Perturbation Theory

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Midwest Undergraduate Computational Chemistry Consortium Conference
February 2012
Motivation

◦ Scientific models can provide us with a quantitative understanding of the natural world
◦ Comprehensible, accurate models are essential to advancing science and understanding the universe
◦ This presentation will introduce a model for chemical bonding and molecular vibrations
Potential Energy Surfaces

- Potential Energy Surfaces (PES) are chemists’ models for reactivity
  - Provide information about transition states, reaction pathways, and relative energies of products and reactants
- Mathematical construct
  - A PES is a potential energy function of the form $V(q_1, q_2, \ldots q_{3N-6})$
  - $q_i$ are molecular internal coordinates (e.g. bond lengths and angles)
- How do you find a PES if you can’t measure it directly?
  - Experiment: Measure vibrational levels
  - Theory: Compute $V(q_1, q_2, \ldots q_{3N-6})$
- Goal: Connect experiment and theory by calculating vibrational levels from $V$

J. Harvey, University of Bristol,
http://www.chm.bris.ac.uk/pt/harvey/msci_pract/back_qm.html
Molecular Motion

- Molecules translate, rotate, and vibrate
- Only vibrations will be considered
  - Vibrations involve changes in the internal coordinates of atoms, whereas rotations and translations do not
  - Therefore vibrations are the coordinates of PES
- Molecules will be treated as anharmonic oscillators
  - The harmonic oscillator gives the zero-order model
- There are $3N-6$ degrees of vibrational freedom, where $N$ is the number of atoms in the molecule

Comparison in one dimension of harmonic (parabolic curve) and anharmonic (semi-parabolic curve) oscillators and their vibrational energy levels.

The potential energy function $V$ that will be used is

$$V = \frac{1}{2} hc \sum_k \omega_k q_k^2 + hc \sum_{klm} \frac{1}{3!} \phi_{klm} q_k q_l q_m + hc \sum_{klmn} \frac{1}{4!} \phi_{klmn} q_k q_l q_m q_n + \ldots$$

- Theory computes the $\omega$’s and $\Phi$’s, the frequencies and force constants, respectively

- In order to relate the $\omega$’s and $\Phi$’s to the vibrational levels mathematically, the Schrödinger equation must be solved…
Schrödinger Equation

\[ H\Psi = E\Psi \]

- **Schrödinger’s Expression:**
  \[
  \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right)\Psi(x) = E\Psi(x)
  \]

- **Heisenberg’s Expression:**
  \[
  \begin{bmatrix}
  H_{aa} & H_{ab} & \cdots \\
  H_{ba} & H_{bb} & \\
  \vdots & & H_{cc} \\
  \end{bmatrix}
  \begin{pmatrix}
  c_1 \\
  c_2 \\
  c_3 \\
  \vdots
  \end{pmatrix}
  =
  E
  \begin{pmatrix}
  c_1 \\
  c_2 \\
  c_3 \\
  \vdots
  \end{pmatrix}
  \]

- **Mathematically Equivalent:**
  \[ \Psi(x) = c_1\psi_a + c_2\psi_b + c_3\psi_c + \ldots \]
  - Eigenfunction \( \Psi(x) \) is a linear combination of basis functions

- The matrix method is implemented in this derivation because it is easier to implement on computers
Diagonalization of the Hamiltonian

- In the matrix method, solving the Schrödinger equation is equivalent to diagonalizing the Hamiltonian

\[ THT^{-1} = \Lambda = \begin{bmatrix} E_1 & 0 & 0 & \ldots \\ 0 & E_2 & 0 & 0 \\ 0 & 0 & E_3 & 0 \\ \vdots & 0 & 0 & \ddots \end{bmatrix} \]

- \( T \) is a unitary matrix whose rows are the coefficients of the basis functions of \( H \)
- \( \Lambda \) is a diagonal matrix whose diagonal corresponds to the energy eigenvalues of \( H \)
Approximate Solutions

• The Schrödinger equation is not exactly soluble for two main reasons:
  ◦ The vibrational Hamiltonian is infinite-dimensional
  ◦ There are both large and small interactions between harmonic oscillator basis functions
    • Large interactions involve resonances between vibrational modes
    • Small interactions between states are anharmonicities
• Thus, a means of approximately solving the Schrödinger equation must be used…
Solving the Schrödinger Equation via Higher Order Van Vleck Perturbation Theory

- Define the Hamiltonian as an infinite expansion and truncate after a certain order

\[ \hat{H} = H^o + \lambda \hat{H}' + \lambda^2 \hat{H}'' + ... \]

- \( \lambda \) is an ordering parameter (and is usually set to one for simplicity)
- Second-order Van Vleck perturbation theory will be used here
- Define the transformation matrix

\[ T = e^{i\lambda \bar{S}} = 1 + i\lambda \bar{S} - \frac{\lambda^2}{2} \bar{S}^2 + ... \]

- Carry out the transformation

\[ T \hat{H} T^{-1} = \tilde{H} = \tilde{H}^o + \lambda \tilde{H}' + \lambda^2 \tilde{H}'' + ... \]
Why Use VVPT?

- Van Vleck perturbation theory treats both large and small interactions
  - First order PT does not treat interactions between states
  - Second order PT only treats small interactions
  - VVPT treats large and small interactions differently, thereby accounting for the complexities of molecules
  - Selection rules make infinite sums finite
Solving the Schrödinger Equation via Perturbation Theory

- First order PT accounts only for corrections to a state itself

\[ \tilde{H}_{aa} = H_a^0 + H'_a \]

- Second order PT accounts for small interactions between states

\[ \tilde{H}_{aa} = H_a^0 + H'_a + H''_a + \sum_{\gamma} \frac{H'_{a\gamma}H'_{\gamma a}}{E_a^0 - E_\gamma^0} \]

- Van Vleck PT accounts for both small and large interactions between states

\[ \tilde{H}_{ab} = H^0 + H'_a + H''_a + \frac{1}{2} \sum_{\gamma} \left[ \frac{H'_{a\gamma}H'_{\gamma b} + H'_{a\gamma}H'_{\gamma b}}{E_a^0 - E_\gamma^0} + \frac{H'_{a\gamma}H'_{\gamma b}}{E_b^0 - E_\gamma^0} \right] \]
Context of Derivation

- Two attempts have been made in the literature to use Van Vleck perturbation theory to describe large interactions in a general fashion, but...
  - …Both are in error: One author provided an incorrect derivation, and the other did not provide one
  - Both papers contain expressions fraught with typographical errors
- Since there are incorrect equations in the literature, scientists have access to several inconsistent equations describing the same quantities
- My work has involved…
  - thoroughly investigating underlying assumptions
  - developing a complete, accurate expression containing all terms as well as a simplified one, in which neglected terms are identified
- Van Vleck perturbation theory has been used in a case-by-case manner to arrive at a result
  - I seek a general method to calculate vibrational energy levels from a potential energy surface
WARNING: Take two ibuprofen tablets before proceeding.
On-Diagonal Matrix Elements

\[ \tilde{H} = H^0 + H'_{aa} + H''_{aa} + \sum_{\gamma} \frac{H'_{a\gamma} H'_{\gamma a}}{E^0_a - E^0_{\gamma}} \]

\[
= \hbar c \sum_k \omega_k \left( v_k + \frac{1}{2} \right) + \frac{1}{16} \hbar c \sum_k \phi_{kkkk} \left( v_k + \frac{1}{2} \right) \left( v_k + \frac{1}{2} \right) + \frac{1}{4} \hbar c \sum_{k\neq l} \phi_{kkll} \left( v_k + \frac{1}{2} \right) \left( v_l + \frac{1}{2} \right) \\
+ \sum_\alpha \sum_{kl} \left( \frac{\omega_l + \omega_k}{\omega_k} \right)^2 \left( v_k + \frac{1}{2} \right) \left( v_l + \frac{1}{2} \right) \\
- \hbar c \sum_k \frac{1}{16} \phi_{kkll}^2 \left( 8 \omega_k^2 - 3 \omega_l^2 \right) \left( v_k + \frac{1}{2} \right) \left( v_l + \frac{1}{2} \right) - \hbar c \sum_k \frac{5}{4} \phi_{kkll}^2 \omega_k \left( v_k + \frac{1}{2} \right)^2 \\
- \hbar c \sum_{k \neq m} \frac{\phi_{kkkl}^2}{2N_{kkll}} \omega_k \left( \omega_k - \omega_l - \omega_m \right) \left( v_k + \frac{1}{2} \right) \left( v_l + \frac{1}{2} \right) - \hbar c \sum_{k \neq m} \frac{1}{2N_{kkll}} \phi_{kkkl} \phi_{kkmm} \left( v_k + \frac{1}{2} \right) \left( v_l + \frac{1}{2} \right) \\
- \hbar c \sum_{k \neq m} \frac{\phi_{kkll}^2}{2N_{kkll}} \left( 4 \omega_k^2 - \omega_l^2 - \omega_m^2 \right) \left( v_k + \frac{1}{2} \right) \left( v_l + \frac{1}{2} \right) - \hbar c \sum_k \frac{1}{4} \phi_{kkll} \phi_{kkmm} \left( v_k + \frac{1}{2} \right) \left( v_l + \frac{1}{2} \right) \\
+ \hbar c \sum_k \frac{3}{64} \phi_{kkll} \omega_l \left( \omega_k + \omega_l + \omega_m \right) - \hbar c \sum_k \frac{7}{576} \phi_{kkll}^2 - \hbar c \sum_k \frac{1}{4} \phi_{kkll} \omega_k \omega_l \omega_m \\
\]

where \[ N_{klm} = (\omega_k + \omega_l + \omega_m)(\omega_k - \omega_l - \omega_m)(\omega_k - \omega_l + \omega_m)(\omega_k + \omega_l - \omega_m) \]
Second-Order Off-Diagonal Matrix Elements for a 2-2 Resonance

\[
\langle n_k + 1, n_l + 1, n_m, n_n | \tilde{H} | n_k, n_l, n_m + 1, n_n + 1 \rangle = \sum_{klm} \frac{K_{kl;mn}}{4} [(n_k + 1)(n_l + 1)(n_m + 1)(n_n + 1)]^{1/2}
\]

where

\[K_{kl;mn} = \phi_{klmn}\]

\[+ 2 \sum_\alpha B_\alpha \left[ \frac{\zeta_\alpha \zeta_\alpha (\omega_k - \omega_l)(\omega_m - \omega_n) - \zeta_\alpha \zeta_\alpha (\omega_k + \omega_m)(\omega_l + \omega_n) - \zeta_\alpha \zeta_\alpha (\omega_k + \omega_n)(\omega_l + \omega_m)}{(\omega_k \omega_l \omega_m \omega_n)^{1/2}} \right]\]

\[- \frac{1}{4} \sum_r \phi_{klr} \phi_{mn} \cdot \left[ \frac{1}{(\omega_k + \omega_l + \omega_r)} + \frac{1}{(\omega_m + \omega_n + \omega_r)} + \frac{1}{-\omega_k - \omega_l + \omega_r} + \frac{1}{-\omega_m - \omega_n + \omega_r} \right]\]

\[- \frac{1}{4} \sum_r \phi_{kmr} \phi_{ln} \cdot \left[ \frac{1}{(\omega_k - \omega_m + \omega_r)} + \frac{1}{(\omega_l - \omega_n + \omega_r)} + \frac{1}{-\omega_k + \omega_m + \omega_r} + \frac{1}{-\omega_l + \omega_n + \omega_r} \right]\]

\[- \frac{1}{4} \sum_r \phi_{kmr} \phi_{ln} \cdot \left[ \frac{1}{(\omega_k - \omega_n + \omega_r)} + \frac{1}{(\omega_l - \omega_m + \omega_r)} + \frac{1}{-\omega_k + \omega_n + \omega_r} + \frac{1}{-\omega_l + \omega_m + \omega_r} \right]\]

- Red circles identify denominators where resonances could occur, i.e. where the denominator could be zero
- Orange circles identify force constants
Notes on Equations

- Evaluated using harmonic oscillator matrix elements
- Describe vibrational energy levels of polyatomic molecules
- Written in non-restrictive summations
  - Non-restrictive summations involve summing over all possible combinations of vibrational modes
  - Restrictive summations include only one of each combination of modes
Comparing Theory and Experiment

- The vibrational energy levels of the theoretical PES can be compared to spectroscopically measured vibrational energy levels.
- Force constants $\omega_k$, $\Phi_{klm}$, and $\Phi_{klmn}$ were calculated by finite differences using the aug-cc-pVTQ basis set and CCSD(T) method.
### Comparison - H$_2$CO

<table>
<thead>
<tr>
<th>Value</th>
<th>VPT2 (2$^{nd}$-Order PT)</th>
<th>VPT2+K (VVPT)</th>
<th>Experiment</th>
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<tbody>
<tr>
<td>$\omega_1$</td>
<td>2933.7</td>
<td>2933.7</td>
<td>2927.8</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>$\omega_6$</td>
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<td>1268.0</td>
<td>1277.2</td>
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<tr>
<td>$x_{11}$</td>
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<td>-32.0</td>
<td>-27.3</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>$x_{66}$</td>
<td>-2.0</td>
<td>-2.0</td>
<td>-2.7</td>
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<tr>
<td>$K_{26,5}$</td>
<td>-</td>
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<tr>
<td>$K_{11,55}$</td>
<td>-</td>
<td>-141.9</td>
<td>-145.3</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>139.4</td>
<td>20.9</td>
<td>-</td>
</tr>
<tr>
<td>% Error</td>
<td>1.4</td>
<td>0.2</td>
<td>-</td>
</tr>
</tbody>
</table>

- VVPT yields more accurate results than second-order perturbation theory for molecules with large interactions (resonances)
Progress Report

- Some difficulties have been encountered in using non-restrictive summations in the on-diagonal expressions
  - Each step in the derivation is being coded into a computer program in order to validate each step and to analyze the equations’ behavior
- These programs will be applied to several molecules to determine their vibrational energy levels
- Once the equations have been finalized and some sample applications are developed, a manuscript will be published (It is currently in the works)
Future Work

- Publish corrected equations with comprehensive derivations
- Apply computer programs to several molecules
- Compare results to results of other methods (e.g. second-order perturbation theory)
- Define new computational technique for vibrational states (VPT2+K)
- Work with Gaussian and WebMO developers to integrate VPT2+K into software
Acknowledgements

- Dr. Polik
- Howard Dobbs
- John D., Kent K., and former Polik group members
- Hope College Chemistry Department
- Dean of Natural and Applied Sciences
- National Science Foundation