

Symmetry and Potential Curves

- Consider a diatomic molecule. The energy of a given electronic state as a function of internuclear distance r is the potential energy curve for that state.
- From symmetry considerations we can show that these curves cross only if they are of different symmetries.
- What are the requirements for curves $E_1(r)$ and $E_2(r)$ to cross? At a crossing point r_c we must have $E_1(r_c) = E_2(r_c)$, and also that $H_{12}(r_c) = 0$, where H_{12} is the matrix element of the Hamiltonian between the two states.



Curve Crossing in Diatomics

- We thus have *two* conditions to satisfy simultaneously, but we have only one parameter (r).
- If the two states are of different symmetries, $\Gamma(\Psi_1) \neq \Gamma(\Psi_2)$, then $H_{12}(r) = 0$ at *all* values of r . Hence if at some point $E_1(r) = E_2(r)$, the two curves will cross.
- If $\Gamma(\Psi_1) = \Gamma(\Psi_2)$, then there is no symmetry reason why H_{12} should vanish. It *may* vanish at some distance, but it is improbable that this will coincide with a point where $E_1(r) = E_2(r)$.
- Other than accidental degeneracy, then, curves of the same symmetry cannot cross one another.
- This means that the dissociation limits of any diatomic molecular state can be determined unambiguously.



Diatomic Potential Curves

- *Correlation diagrams* for molecular electronic states can be constructed following Wigner and Witmer.
- Construct molecular wave functions as products of atomic wave functions, generate spin eigenfunctions and symmetry-adapted many-electron functions.
- If the atomic states are different (different atoms or different states of the same atom) the spin is easily determined: use tables for the spatial symmetry.
- Some subtleties when inversion symmetry is present.
- Sidebar: States of N_2 .



Surfaces in Polyatomic Molecules

- The noncrossing rule must be modified — for any polyatomic we have at least three geometric parameters and there is no reason why we cannot simultaneously arrange that

$$\begin{aligned}E_1(\vec{r}) &= E_2(\vec{r}) \\ H_{12}(\vec{r}) &= 0\end{aligned}$$

even when $\Gamma(\Psi_1) = \Gamma(\Psi_2)$.

- In general, for a potential surface in n dimensions, there will be a “line” in $n - 2$ dimensions along which the surfaces cross.
- This was not well understood for a long time. In two dimensions the crossing point is a *conical intersection*, and the wave function changes phase on a trajectory around the intersection.



Surfaces in Polyatomic Molecules

- Jahn-Teller Theorem: a stationary point on a potential energy surface that corresponds to a degenerate state of a nonlinear polyatomic molecule is not even a local minimum.
- That is, the geometry of a degenerate state of a nonlinear polyatomic molecule will distort, lowering the symmetry until the state is no longer degenerate.
- This is all we know from symmetry. Which distortions will occur (when several are possible) is not determined, for example. This requires calculation or hand-waving.
- Sidebar: $\text{Cu}(\text{H}_2\text{O})_6^{2+}$.



Surfaces in Linear Molecules

- The situation in the case of linear molecules is less straightforward.
- There is no requirement that degenerate states will distort to lift the degeneracy.
- Some geometric distortions *will* lower the symmetry, but the high symmetry geometry (and degenerate state) may remain a minimum.
- This is the *Renner-Teller* effect.

