Figure 1.1: Potential energy curves $U_a(R)$ for different adiabatic electronic states ϕ_a along the bond distance R of a diatomic molecule (ground and valence states of I_2).
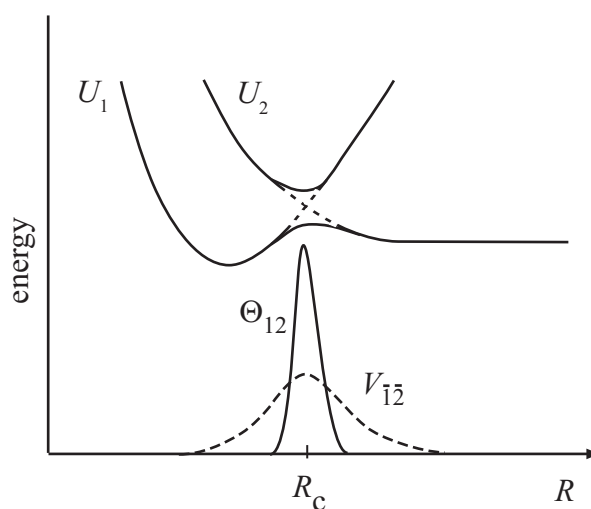

Figure 1.2: Schematic view of adiabatic (solid) and diabatic (dashed) potential energy curves along a nuclear coordinate. For $R \ll R_c$ both potential curves are well separated; the lower and upper diabatic states belong to a bound and repulsive electronic state, respectively, and so do the adiabatic potentials U_1 and U_2. For $R \gg R_c$ the character of the potential curves changes; U_2 corresponds to a bound state and U_1 is repulsive now. This is reflected in the electronic wave functions and therefore in the state couplings shown in the lower part.

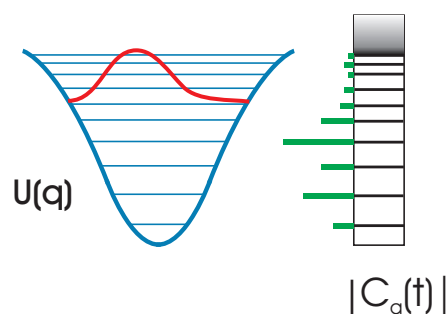$$\Psi(q, t) = \Sigma_a \, c_a(t) \, \phi_a(q)$$

$$U(q)$$

$$|C_a(t)|$$

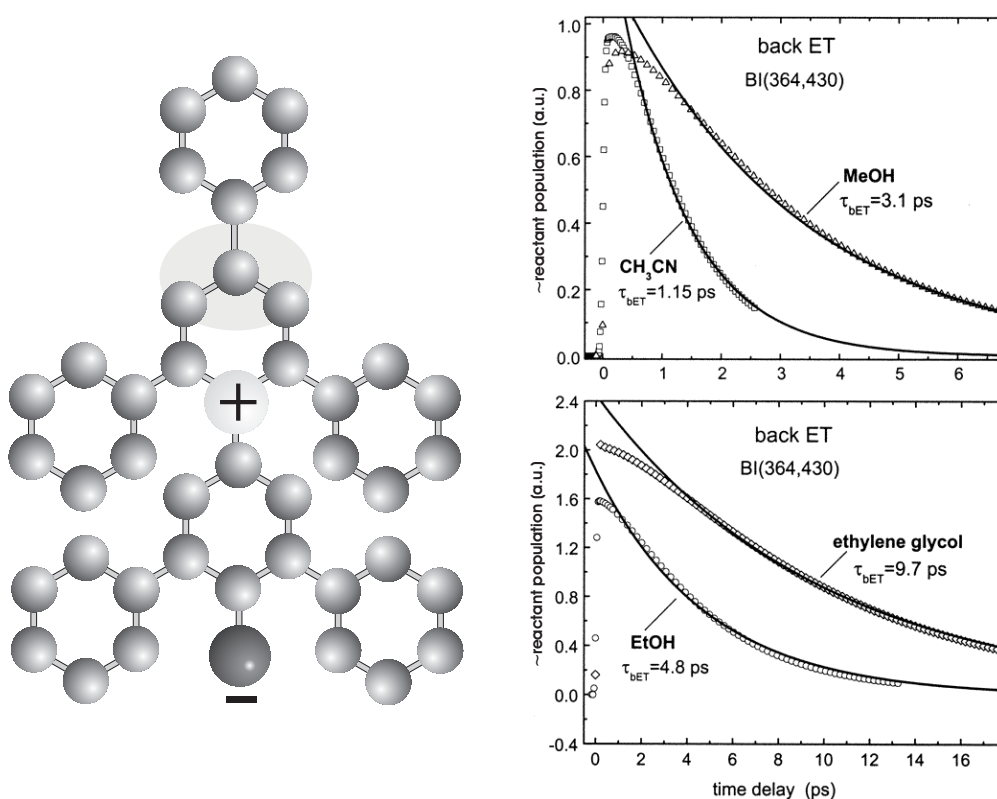Figure 1.3: Wave packet formation and motion in an attractive potential.

Figure 1.4: Ultrafast internal conversion from the S_1 to the S_0–state of the pyridinium N–phenolate dye betaine–30. (Betaine–30 represents a very sensitive solvatochromic probe often used for polarity measurements.) Left panel: molecular structure (carbon atoms are shown in grey, nitrogen in weak grey, and oxygen in black). The ground state is characterized by a large dipole moment mainly according to the charge separation between nitrogen and oxygen. Upon excitation into the S_1–state the dipole moment is reduced since the negative charge moves to a carbon atom (shown by a grey sphere above the nitrogen atom). Right panel: decay of the reactant population (proportional to the transient absorption signal) for different solvents (solid lines are a monoexponential fit of the measured data, from S. A. Kovalenko, N. Eilers–König, T. A. Senyushkina, and N. P. Ernsting, J. Phys. Chem. A **105**, 4834 (2001)).
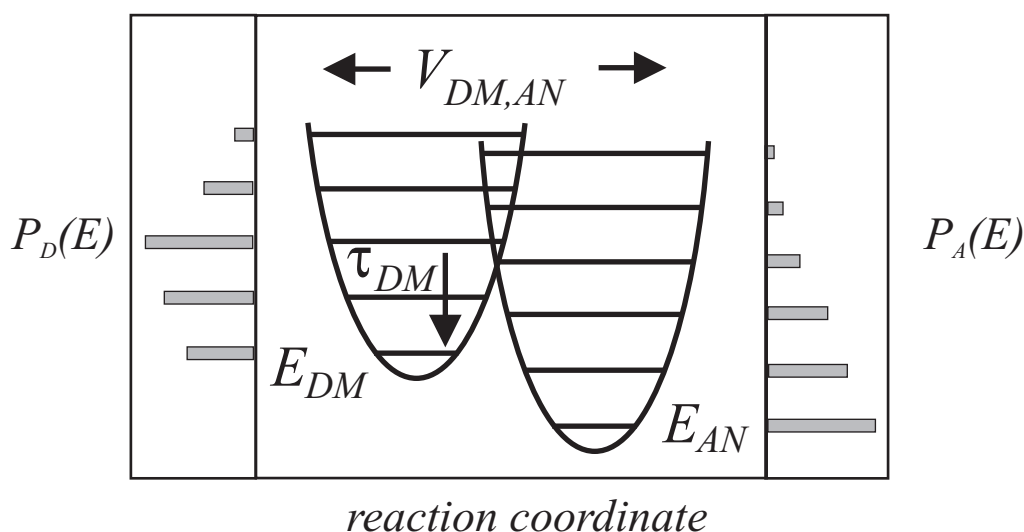
Figure 1.5: Electronic transitions in a system of two coupled PES with electron donor vibrational levels E_{DM} and electron acceptor vibrational levels E_{AN} (the coupling matrix elements $V_{DM,AN}$ are also drawn). Left scheme: population P_D of the donor levels after optical excitation, right scheme: population P_A of the acceptor levels after relaxation took place. (If both spectra are degenerated a direct transfer from a selected level E_{DM} to a level E_{AN} becomes possible, probably connected with a back transfer. If degeneracy is absent a set of different levels is coupled simultaneously.)
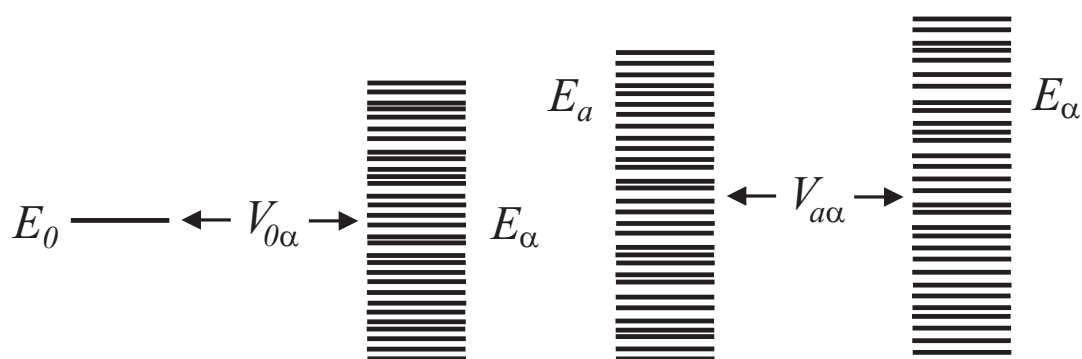

Figure 1.6: Level schemes used to derive the Golden Rule of Quantum Mechanics. Left: coupling of a single state $|0\rangle$ to the manifold of states $|\alpha\rangle$, right: coupling of the manifold of initial states $|a\rangle$ to the manifold of final states $|\alpha\rangle$.