2. Unstable Diatomic Molecule

In a diatomic molecule, the interaction between the atoms depends on their electronic configuration. It is conceivable that a molecule is stable if one of the atoms is electronically excited, and unstable if both atoms are in their ground state. We study here such a scheme, and we focus in particular on the dissociation of the molecule when the initially excited atom decays to its ground state.

2.1 Preliminaries

2.1.1. Consider a particle of mass $M$ moving along the $x$ axis and placed in the potential $V_1(x)$:

$$V_1(x) = +\infty \quad \text{for } x \leq x_0$$

$$= 0 \quad \text{for } x > x_0.$$ 

Let $\varphi_k(x)$ be a stationary solution of the Schrödinger equation with energy $E$. It can be written, for $x > x_0$, as

$$\varphi_k(x) = e^{ik(x-x_0)} + B e^{-ik(x-x_0)}.$$ 

(a) Express $k$ in terms of $E$.
(b) What is the value of $\varphi_k(x)$ for $x \leq x_0$?
(c) What is the value of $B$?
(d) Write the general solution of the Schrödinger equation in terms of the functions $\varphi_k(x)$.

2.1.2. We now consider a particle of mass $M$ moving along the $x$ axis and placed in the potential $V_2(x)$:

$$V_2(x) = +\infty \quad \text{for } x \leq x_0$$

$$= V_0 + M\omega_0^2 x^2/2 \quad \text{for } x > x_0.$$ 

where $V_0$ is a constant.

(a) What is the wave function for $x \leq x_0$?
(b) Express the eigenfunctions $\chi_n(x)$ of the Hamiltonian in terms of the normalized Hermite functions $\Phi_n(y) = c_n e^{y^2/2} \frac{d^n}{dy^n} e^{-y^2}$.
(c) What are the corresponding energy levels?
2.2 A Molecule Which Is Only Stable in Its Excited States

Consider a diatomic molecule $XY$. Let $x$ be the distance between the nuclei (or between the centers of gravity) of the two atoms $X$ and $Y$.

The potential energy between the two atoms depends on the excitation state of the electrons. Let $V(x)$ be this potential energy (for a given electronic state). Then the (lowest) energy levels of the relative motion of the two atoms are obtained by solving the one-dimensional Schrödinger equation

$$-\frac{\hbar^2}{2M} \frac{d^2}{dx^2} \varphi(x) + V(x) \varphi(x) = E \varphi(x),$$

(2.1)

where $M$ is the reduced mass $M = M_X M_Y/(M_X + M_Y)$.

Let $V = V_g(x)$ be the potential energy when the electrons are in the ground state and $V = V_e(x)$ the potential energy when one electron is in its first excited state. The molecule is assumed to be such that $V_e(x)$ has a minimum at $x = x_0$ whereas $V_g(x)$ is a decreasing function of $x$, such as shown in Fig. 2.1.

![Potential energy](image)

**Fig. 2.1.** Variations of the two potentials $V_g$ and $V_e$ as a function of the interatomic distance $x$.

**2.2.1.** Indicate without calculation whether the stationary states of equation (2.1) are bound states or scattering states (in which case the molecule does not have a stable configuration) in the two cases $V = V_e(x)$ and $V = V_g(x)$.

What conclusion may be drawn concerning the stability, or the existence, of the molecule $XY$ when the electrons are in the ground state or in the excited state?

In your opinion, of the three molecules $N_2$, $He_2$, $HCl$, which one could be described by this type of model?