

## Separation of sub-systems

We will often encounter the need to separate the degrees of freedom in our Hamiltonian into different parts or sub-systems. For instance, consider the Hamiltonian for a system that has been divided into sub-systems 1 and 2:

$$H = H_1(p, q) + H_2(P, Q) \quad (1.1)$$

These subsystems refer to completely separable degrees of freedom, with no interactions between them. Examples include separation of electronic and nuclear degrees of freedom, and separation of a system from a bath. If so we can find solutions to the TISE for each subsystem:  $H_1|\chi_n\rangle = E_n|\chi_n\rangle$  and  $H_2|\varphi_M\rangle = E_M|\varphi_M\rangle$  where  $n$  and  $M$  are quantum numbers for eigenstates of the two subsystems. The state of the system can be represented in terms of product states in the two sub-systems:  $|\psi\rangle = |\chi_n\varphi_M\rangle$ , and the energy is simply additive in the system

$$H|\psi\rangle = (H_1 + H_2)|\chi_n\varphi_M\rangle = (E_n + E_M)|\chi_n\varphi_M\rangle. \quad (1.2)$$

The state of the system can be expressed in terms of independent expansion coefficients in each basis:

$$|\psi\rangle = \sum_{n,M} c_n c_M |\chi_n \varphi_M\rangle \quad (1.3)$$

The time dependence of this system is simply expressed as independent evolution of each subsystem under its own TDSE, for instance

$$i\hbar \frac{\partial |\chi_n\rangle}{\partial t} = H_1 |\chi_n\rangle. \quad (1.4)$$

Now, consider if there is also a coupling or interaction between these sub-systems:

$$H' = H_1(p, q) + H_2(P, Q) + V_{12}(p, P, q, Q) \quad (1.5)$$

The interaction  $V_{12}$  will depend on operators of both systems. The product states are not eigenstates of  $H'$ , as the eigenstates of  $H_0$  become entangled with those of  $H_1$ . Nonetheless, the product states still form a complete basis by which to express the state of the system:

$$|\psi'\rangle = \sum_{n,M} C_{n,M} |\chi_n \varphi_M\rangle. \quad (1.6)$$

However  $C_{n,M} \neq c_n c_M$ , generally speaking. To the extent that the interaction is weak relative to the internal energy scale of  $H_1$  and  $H_2$ , the degree of mixing is small and the corrections to the energy eigenvalues and eigenstates can be addressed with perturbation theory.

It is common that we wish to focus our attention on one subsystem  $H_1$ , and that we have no interest in specifying the state of system 2. Rather we wish to treat the *influence* of

state 2 on state 1 as an interaction potential. That is, we wish to replace eq. (1.5) with one of the form

$$H = H_0 + V(t) \quad (1.7)$$

When can we do this, and what does it mean to functionally remove one subsystem from consideration? Working in the product basis  $|\psi\rangle = |\chi_n \varphi_M\rangle$  and substituting eq. (1.5) into the TDSE, we can write

$$i\hbar |\varphi_M\rangle \frac{\partial |\chi_n\rangle}{\partial t} + i\hbar |\chi_n\rangle \frac{\partial |\varphi_M\rangle}{\partial t} = |\varphi_M\rangle H_1 |\chi_n\rangle + |\chi_n\rangle H_2 |\varphi_M\rangle + V_{12} |\chi_n\rangle |\varphi_M\rangle \quad (1.8)$$

Then left multiplying by  $\langle \varphi_M |$  and making use of eq. (1.4), we can write

$$i\hbar \frac{\partial |\chi_n\rangle}{\partial t} = [H_1 + \langle \varphi_M | V_{12} | \varphi_M \rangle] |\chi_n\rangle \quad (1.9)$$

This is equivalent to the TDSE for a Hamiltonian of form (1.7) where the external interaction  $V(t) = \langle \varphi_M | V_{12} | \varphi_M \rangle$  comes from integrating the 1-2 interaction over sub-space 2. This is also known as tracing over the system 2 degrees of freedom.

Thus when implementing one is making a time-dependent mean field approximation, in which the influence of system 2 on system 1 is treated as an average level. Furthermore, for an ensemble of molecules, there is a uniform action of system 2 on all molecules in system 1 under the average form of the perturbation.