

## 16.4: Wavepackets

In an attempt to combine the attributes and strengths of classical trajectories, which allow us to "watch" the motions that molecules undergo, and quantum mechanical wavefunctions, which are needed if interference phenomena are to be treated, a hybrid approach is sometimes used. A popular and rather successful such point of view is provided by so called **coherent state wavepackets**.

A quantum mechanical wavefunction  $\psi(\mathbf{x}|\mathbf{X}, \mathbf{P})$  that is a function of all pertinent degrees of freedom (denoted collectively by  $\mathbf{x}$ ) and that depends on two sets of parameters (denoted  $\mathbf{X}$  and  $\mathbf{P}$ , respectively) is defined as follows:

$$\psi(\mathbf{x}|\mathbf{X}, \mathbf{P}) = \prod_{k=1}^N e^{\left[ \frac{iP_k x_k}{\hbar} - \frac{(x_k - X_k)^2}{4\langle \Delta x_k \rangle^2} \right]} \frac{1}{\sqrt{2\pi\langle \Delta x_k \rangle^2}}$$

Here,  $\langle \Delta x_k \rangle^2$  is the uncertainty

$$\langle \Delta x_k \rangle^2 = \int |\psi|^2 (x_k - X_k)^2 d\mathbf{x}$$

along the  $k^{\text{th}}$  degree of freedom for this wavefunction, defined as the mean squared displacement away from the average coordinate

$$\int |\psi|^2 x_k d\mathbf{x} = X_k.$$

So, the parameter  $X_k$  specifies the **average value** of the coordinate  $x_k$ . In like fashion, it can be shown that the parameter  $P_k$  is equal to the **average value** of the momentum along the  $k^{\text{th}}$  coordinate:

$$\int \psi^* \left( -i\hbar \frac{\partial}{\partial x_k} - P_k \right) \psi d\mathbf{x} = P_k$$

The uncertainty in the momentum along each coordinate:

$$\langle \Delta p_k \rangle^2 = \int \psi^* \left( -i\hbar \frac{\partial}{\partial x_k} - P_k \right)^2 \psi d\mathbf{x}$$

is given, for functions of the coherent state form, in terms of the coordinate uncertainty as

$$\langle \Delta p_k \rangle^2 \langle \Delta x_k \rangle^2 = \frac{\hbar^2}{4}$$

Of course, the general Heisenberg uncertainty condition

$$\langle \Delta p_k \rangle^2 \langle \Delta x_k \rangle^2 \geq \frac{\hbar^2}{4}$$

limits the coordinate and momentum uncertainty products for arbitrary wavefunctions. The coherent state wave packet functions are those for which this **uncertainty product is minimum**. In this sense, coherent state wave packets are seen to be as close to classical as possible since in classical mechanics there are no limits placed on the resolution with which one can observe coordinates and momenta

These wavepacket functions are employed as follows in the most straightforward treatments of combined quantal/classical mechanics:

1. Classical trajectories are used, as described in greater detail above, to generate a series of coordinates  $X_k(t_n)$  and momenta  $P_k(t_n)$  at a sequence of times denoted  $\{t_n\}$ .
2. These classical coordinates and momenta are used to **define** a wavepacket function as written above, whose  $\mathbf{X}_k$  and  $\mathbf{P}_k$  parameters are taken to be the coordinates and momenta of the classical trajectory. In effect, the wavepacket moves around "riding" the classical trajectory's coordinates and momenta as time evolves
3. At any time  $t_n$ , the quantum mechanical properties of the system are computed by forming the expectation values of the corresponding quantum operators for a wavepacket wavefunction of the form given above with  $X_k$  and  $P_k$  given by the

classical coordinates and momenta at that time  $t_n$ .

Such wavepackets are, of course, simple approximations to the true quantum mechanical functions of the system because they do not obey the Schrödinger equation appropriate to the system. They should be expected to provide accurate representations to the true wavefunctions for systems that are more classical in nature (i.e., when the local de Broglie wave lengths are short compared to the range over which the potentials vary appreciably). For species containing light particles (e.g., electrons or H atoms) or for low kinetic energies, the local de Broglie wave lengths will not satisfy such criteria, and these approaches can be expected to be less reliable. For further information about the use of coherent state wavepackets in molecular dynamics and molecular spectroscopy, see E. J. Heller, *Acc. Chem. Res.* 14, 368 (1981).

*This completes our treatment of the subjects of molecular dynamics and molecular collisions. Neither its depth nor its level was at the research level; rather, we intended to provide the reader with an introduction to many of the theoretical concepts and methods that arise when applying either the quantum Schrödinger equation or classical Newtonian mechanics to chemical reaction dynamics. Essentially none of the experimental aspects of this subject (e.g., molecular beam methods for preparing "cold" molecules, laser pump/probe methods for preparing reagents in specified quantum states and observing products in such states) have been discussed. An excellent introduction to both the experimental and theoretical foundations of modern chemical and collision dynamics is provided by the text **Molecular Reaction Dynamics and Chemical Reactivity** by R. D. Levine and R. B. Bernstein, Oxford Univ. Press (1987).*

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