Use of potential energy surfaces (PES) in spectroscopy and reaction dynamics

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Introduction

Potential energy surfaces (PES) play very important role in analysis of reaction dynamics and molecular structures studies. The Born-Oppenheimer approximation is invoked in molecular system to create PES. In computational chemistry determination of potential energy surfaces, allows determination of energy minima and transition states. Once a reasonable PES is constructed, vibrational spectra and reaction rate can be calculated and predicted. In this paper some potential energy surfaces for simple molecular systems will be introduced and use of PES in spectroscopy and reaction dynamics is demonstrated.

PES can be constructed based on Born-Oppenheimer approximation which regards electrons run much faster than nucleus and rests on the fact the nucleus are much more massive than electrons, and allows us to say that the nucleus are nearly fixed with respect to electron motion. From figure 1 we can get the connection of PES between relevant theory and experiment. By vib-rotational calculations it’s convenient to predict spectroscopy concerned. As well as by finding transition state and minima including local minima and global minimum we can realize and determine chemical reaction dynamics[1]. These two main aspects will be discussed and studied in this paper. Besides application in spectroscopy[2] and reaction dynamics PES is involved in cross section which is used to study theories of molecular collision due to molecular beams applied widely. Furthermore, it’s also applied in in-deep study for themophysical properties in the case of statistical mechanics to solve the problem of macroscopic coefficients.

Figure 1 Connection between PES and theory, experiment
Part I use of PES in spectroscopy

As it is known, a system including N atoms is uniquely defined by 3N coordinates x, y, z for each atom. However we don’t take overall translation and overall rotation into account. Therefore, freedom degree of a PES has 3N-6 coordinates for Non-linear molecules and 3N-5 for Linear molecules[3]. Generally, we call PES as potential energy curve when N equals 2, and potential energy hypersurfaces while N≥3. To simplify this conception all potential will be called as Potential energy surface (PES). PES is a function of coordinates as followed:

\[ U(q_1) \]  
\[ U(q_1, q_2) \]  
\[ U(q_1, q_2, q_3) \]  
\[ U(q_1, q_2, q_3, \ldots q_n) \]  

\[ q_1, q_2, \ldots \in \{ R_n, \theta_n \} or \{ x_n, y_n, z_n \} \]

The expression of function has many different forms due to different molecular structures as shown in figure2. In fact, it’s difficult to get the real form of function, but people always try to find their function to approach the actual results. Some diatomic potential function will be introduced later.

A specific potential function is determined by a known molecular system. Some popular functions of potential energy surfaces have been established by physics or chemistry scientist. For example a famous one is Morse potential.
Figure 3 shows a typical diatomic potential energy surface. The shape of the valley around a minimum determines the vibrational spectrum. Each electronic state of a molecule has a separate potential energy surface, and the separation between these surfaces yields the electronic spectrum. This is a simple but useful model to study potential energy surface start with something all we have seen.

![Potential energy surface for a diatomic molecule.](image)

Figure 3 Potential energy surface for a diatomic molecule.

In this graph, $R_e$ is an important parameter which means the equalization distance between two atoms as well as $D_e$ is dissociation energy of the AB molecule. The PES has many vibrational and rotational energy levels. This molecule can be excited high energy level by collision of other molecules, electrons, or absorbing photons. Once the energy is enough, the dissociation of molecule can happen, which forms two independent atoms.

![Typical potential energy surface](image)

Figure 4 Typical potential energy surface

In figure 4 one typical 3D PES is shown for a more complicated molecule. This potential energy surface is plot by two coordinates (two angels of bond rotation). Given the angel $\alpha$ is
specific value as 30°, a potential energy curve can be obtained as shown in sub-frame. In fact, this is a result from cutting the object to produce a plane.

\[ D = \frac{\eta^2}{(2m^2R_e^2k)} \] (5)

\[ B_e = \frac{h}{(8\pi^2R_e^3c)} \] (6)

\[ \nu = (1/2\pi)(k/m)^\frac{3}{2} \Rightarrow \omega_e \] (7)

\[ \chi_e\omega_e = \omega_e^2/4D_e \] (8)

Where h is plank constant, K means force constant, M is reduced mass, \( \nu \) vibrational frequency, \( c \) is Light speed, \( R_e \) equals distance between nucleus.

Equations (5)–(8) can be used to determine these very important spectroscopic parameters \( B_e, D, \omega_e, \chi_e \omega_e \) and so on.

As long as these parameters are determined, the energy level we can derivate formula as follow:

\[ E(V, J) = \nu_0 + \omega_e(V+1/2) - \chi_e\omega_e(V+1/2)^2 + BJ(J+1) - DJ^2(J+1)^2 \] (9)

In other way round, if we have obtained spectroscopy from experimental data, we also can determinate a corresponding potential energy surface with spectral constants.

The spectra will be predicted by equations (10) ~ (11) for rotational spectrum and vibrational-rotational spectrum, respectively.

Rotational spectrum \[ \Delta E = E(J', V) - E(J'', V) \] (10)

Vib-rotational spectrum \[ \Delta E = E(J', V') - E(J'', V'') \] (11)

Figure 5 The flow chart to calculate potential energy surface
The flow chat to determine potential energy surfaces is given in figure 5. There are two main methods to calculate potential surface. One is *ab initio* calculation, and the other one is initial guess at parameters of potential surface, which is compared with the result from experimental spectrum by adjusting parameters. Finally, the energy level and wavefunctions can be obtained. *ab initio* is a popular method to calculate electron structure[4]. In this method one performs a large number of electronic structure calculations (which may be very expensive) and then fits the results using a least squares procedure. The reliability of the PES depends on the basis set completeness and how well electron correlation is accounted for. Drawbacks to this method are, the size and the number of calculations necessary to characterize the entire surface is too expensive for large systems, especially when more than the reactant, product, and saddle point regions are important for the dynamics of the system. To make sure that *ab initio* calculations are performed for the most important geometries may require an iterative process in which some type of dynamics calculation is done on a preliminary surface, and the results are analyzed for their sensitivity to various PES regions to determine where further calculations are most important to improve the surface. It is difficult to obtain a good fitting when using general least squares fitting of *ab initio* results unless physically motivated functional forms are used. Table 1 lists some different *ab initio* calculation softwares and simulation programs designed by Agust Kvaran’s group.

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Table 1 *ab initio* calculation and simulation program

Frequently-used functions of potential energy surfaces for diatomics like Lennard-Jones,
Morse, Rydberg, Murrell[5-6] with detail expression are given as equation (12) ~ (15) and Figure 6~7 are the example of PESs simulations for different states and explain possible dissociation channels for HCl.

**Lennard-Jones**

\[ U(R) = 4e \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^{6}, \quad R_e = 2^{1/6} \sigma \]  

(12)

**Morse**

\[ U(R) = D_e \left( 1 - \exp\left[ -\beta(R-R_e) \right] \right)^2 \]  

(13)

**Rydberg**

\[ U(R) = -D_e \left( 1 + \beta (R-R_e) \right) \exp\left[ -g(R-R_e) \right] \]  

(14)

**Murrell**

\[ U(R) = -D_e \left[ 1 + a_1 (R-R_e) + a_2 (R-R_e)^2 + a_3 (R-R_e)^3 \right] \exp\left[ -g(R-R_e) \right] \]  

(15)

Where \( a_1, a_2, a_3, \gamma, \beta \) are adjustable parameters. In the simulation of potential energy surface, at the beginning we guess an initial function shape of PES and adjust relevant parameters to calculate spectra which are used to be compared with experimental spectra[7]. See figure 8~9.
Part II use of PES in reaction dynamics

From a computational point of view, many aspects of chemistry can be reduced to questions about potential energy surfaces (PES). Potential surface of the energy as a function of the molecular geometry show some information on the features. A typical PES has valleys, mountain passes and peaks. Reaction rates can be obtained from the height and profile of the mountain pass separating the valleys of the reactants and products. Molecular structures correspond to the positions of the minima in the valleys on a potential energy surface. Thus, the structure, properties, reactivity, and spectra of molecules can be readily understood in terms of potential energy surfaces. Except in very simple cases, the potential energy surface...
cannot be obtained from experiment instead of computation.

Figure 10 (a) 3D potential energy surface and contour plot  (b) Reaction coordination

R-reactants, Ts-Transition state, I-intermediate, P-productions

A 3D potential energy surface and contour plot are shown in figure 10 (a). There are a few special points be marked on the potential energy surface. Mathematically, each point has its criteria. Minima and saddle point belong to stationary point at which the surface is flat on a PES, but in fact they have different meaning in chemistry[8].

A minimum satisfies this expression

$$\frac{\partial^2 U}{\partial q^2} > 0, \quad \frac{\partial U}{\partial q} = 0$$

for all q

For a transition state (Saddle point)
\[ \frac{\partial^2 U}{\partial q^2} > 0, \quad \frac{\partial U}{\partial q} = 0 \]

for all \( q \), except along the reaction coordinate.

\[ \frac{\partial^2 U}{\partial q^2} < 0 \]

along the reaction coordinate.

From reaction coordination in figure 10(b) we will know how energy changes from reactants to products across transition states. The reaction coordinate always represents the progress of the reaction. The three species of interest, reactants, productions, and the transition state linking these two, are called stationary points. Sometimes there is existence of intermediate for instance, shown in this figure.

A model of reaction \( AB+C\rightarrow BC+A \) is depicted in figure 11 (a) and its 3D PES shown in (b). The lowest-energy pathway linking the two minima, the reaction coordinate or intrinsic reaction coordinate is the path that would be followed by a molecule in going from one minimum to another should it acquire just enough energy to overcome the activation barrier, pass through the transition state, and reach the other minimum.

![Figure 11 (a) Contour diagram](image1)

![Figure 11 (b) 3D potential energy surface](image2)

This model can be used to assign specific chemical reaction. For example:

\[ \text{Br} + \text{HCl}(v) \rightarrow \text{HBr} + \text{Cl} \]

\[ \text{Na} + \text{HF}(v',J') \rightarrow \text{H} + \text{NaF}(v'',J'') \]

\( v =0,1,2... \quad J=0, 1, 2... \)

Besides the above we have mentioned, some different classes contour plot of potential energy surfaces like I shaped, T shaped, H or X shaped are illustrated in figure12.
Figure 12 Different classes of potential energy surfaces in the vicinity of transition states

Figure 13 Calculation in chemical reaction

According to the reaction coordination, the value of $E_a$ can be determined. By using Arrhenius Equation, a calculation of rate constant can be performed.

$$K=Ae^{-E_a/RT}$$

(16)

Where $K$ is rate constant, $A$ is frequency factor, $T$ is temperature, $E_a$ is activation energy, and $R$ is gas constant.

**Conclusion**

Potential energy surfaces are used widely in study of spectroscopy and reaction dynamics, which play a very important and foundational role in chemistry. The properties of molecular system can be determined or calculated after construction of relevant potential energy surfaces. This paper demonstrates the potential energy surface is a very useful and powerful
analysis tool.

References

[5]. P.M.Morse, Phys. Rev.,34, 57(1929)