分子彈性碰撞研究之一

Research in Molecular Elastic Scattering (I)

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目 錄

1. 中 文 摘 要

原子與原子(或分子與分子)發生彈性碰撞時原子核間之相對位置成爲位能變化的函數、通常原子間的位能圖屬於最低層電子能量狀態。

爲了要導出符合實際的學說必須更假設某些部分的省略未簡化其複雜性。原子與原子之間碰撞力可分爲長距離中距離及短距離，各段可以用不同的數學式來描述。每段間所顯示出的用肉眼可見可測量的性質可用來導出位能的數學式。因爲位能數學式中變數愈多導理部分愈呈煩瑣，因此通常位能數學式只用最多含三變數者。

因爲有了省略的假設碰撞力的分段和位能數學式的不能過於煩雜、使得由實驗室測量得出的位能數學式會無獨有偶。另外、變數的數值與所先設的位能數學形式有密切的關連、而且實驗測量的數據與每段位能之間不會有同樣靈敏的關係。所以、位能數學式不會是100％正確的代表原子與原子之間的作用力。

2. Statement of Problem ——

Since the theoretical formulation of the potential function is a formidable problem, it is customary to be determined empirically by assuming some reasonable form for it involving adjustable parameters. The data of cross section from scattering measurements contain more information about intermolecular force than many macroscopic measurements. The purpose of this research is the empircal investigation concerning one to one correspondence between the cross section and atoms of the scattering pair in atomic and molecular scattering.

3. Abstract ——

With the Born-Oppenheimer separation between electronic and nuclear motions, there is a potential energy surface which determines the motion of the nuclei and refers to a single ground electronic state of the system. The introduction of approximations in order to obtain a simplified theory becomes absolutely essential in revealing the physical insight of the interaction energy. If the intermolecular interaction is classified into a long-range, an intermediate-long- range and a short-range forces, different mathematical techniques dealing with the corresponding macroscopic properties can be used in the various regions of molecular forces. In view of the difficulty involved in detailed calculations, it has been customary to employ the conventional 2- or 3-parameter functionalities which are good semi-quantitative models. The non-negligible dependence of the derived potential parameters upon the assumed functionality of the potential, along with the different sensitivity of the various measurements to different parts of the potential, makes the non-uniqueness more pronounced in reconstructing the intermolecular potential.

4. Phenomena ——

Intermolecular forces are responsible for most of the physical and chemical properties of matter. It should be noted that no direct way of measuring intermolecular forces is known. What is genersllly available are measurements of some macroscopically observable quantity having some functional dependence upon inter-molecular forces[1]. The problem, then is to extract information about these forces by analysis of the measurements. The degree of success will depend on the accuracy of both the measurements and the theory connecting the forces to macroscopic properties, and on the sensitivity of this connection.

In almost all cases, the intermolecular potential cannot be reconstructed uniquely from the measured property, even in principle. The intermolecular potential may be regarded as having been mapped onto[2] some macroscopic property. Since the mapping may not have a one- to -one correspondence to the property, the inversion of experimental data need not yield a unique potential. Therefore, it is generally convenient to assume some mathematical form for the potential, and then to determine the parameters of the model by comparison of calculated macroscopic properties with experiment.

Different forms of the assumed empirical potential function lead to slightly different numerical values of $V(r)$[3]. On the other hand, although it seemed reasonable that the use of the inverse-power function should have no serious adverse effect on the derived values of $V(r)$, it was not possible to show this formally since other reasonable empirical functions, such as the exponential, or screened Coulomb, could not be treated analytically to obtain general relations for the total scattering cross section.

Very often, one tries to use cross-sectional data to investigate the unknown law of force.[4,5] There are several ways to do this, The most common way is to assume that the potential takes some simple shape, such as $K \exp(-r/r_0)/r^n$, and to see whether K, r_0 and n can be chosen so as to obtain a fit to the data. The potential can also be represented as a sum of several simple functions suggested by theory. Simple examples

are the(exp-6) potential, an r^{-6} attractive term plus an exponential repulsive term, and the piecewise inverse power function.

The crucial point in the use of potential models is the guidance furnished by theory in the selection of a model in the first place. without some theoretical foundation for a model, the number of reasonable possibility is distressingly large.

5. Reasons ——

The concept of inter-molecular forces and potential energy surfaces is closely related to the Born-Oppenheimer separation between electronic and nuclear motions. It implies that the nuclear motion or the collision process is adiabatic in the Ehrenfest sense. That is, the molecular aggregate or the collision complex can be characterized by a set of electronic quantum numbers; and these quantum numbers do not change during the course of the collision. Corresponding to each set of these quantum numbers, there is a potential energy surface which determines the motion of the nuclei.

There are two causes for the deviations from the Born-Oppenheimer separation. First, coupling terms appear in the kinetic energy when the coordinates are transformed from the laboratory-fixed axes to the molecular axes. And second, the Breit-Pauli relativistic corrections to the electrostatic Hamiltonian lead to spin-spin, spin-orbit, and other magnetic coupling terms.

There are two kinds of correction terms for the coupling of the electronic and nuclear motions. The energy corrected for the diagonal coupling terms by shifting the energy levels is called the adiabatic approximaion, which gives the best possible potential energy curves and surfaces. The adiabatic approximation to the energy is an upper bound to the true energy since it can be expresed as the expectation value to the correct Hamiltonian for the molecule evaluated with an approximate wave function.

It becomes absolutely essential to introduce approximations to obtain a simplified theory which is qualitatively correct and which indicates the general form of the interaction energy. An approximation-calculation, even if very crude, often reveals trends and relationships which are usually obscured in an accurate but complex calculation. Also physical insight is often obtained from a simple theory, but lost in an elaborate theory.

It is often convenient to classify an intermolecular interaction as a long-range, a short-range, or an intermediate-range force; this classification results largely from the different mathematical techniques[6] required in the various regions of molecular forces.

1. Long-range forces

The simplest example of this is the long range interaction between molecules with non-zero multiple moments. The dependence of the interaction energy on separation distance and molecular orientation is fairly simple and is, externally, the same in classical and quantum mechanics. The simplest long-range force is caused by the induction of a multipole in one molecule by the permanent multipoles of some other molecule. An important interaction of this sort is the dipole-induced dipole interaction (varying as r^{-6}).

Usually the $-C_6/r^6$ London dispersion energy is measured as the longest-range component

of the intermolecular potential. Thermal energy measurements of quantum total cross sections have been made for a large number of systems involving rare gases, alkali atoms, etc., with an accuracy of the order of 10%, yielding the long range attractive constant C_6 within ca. 25%.

2. Intermediate-range forces

The long-range forces first appear in a second order perturbation with unsymmetrized wave functions, whereas short-range forces appear in a first order calculation with symmetrized wave functions. At some intermediate separations, the two calculated energies will be comparable, although they have been obtained by mutually inconsistent approximations. Unfortunately the semi-empirical method involves taking explicit account of all the electrons, and so such calculations have never been carried beyond two He atoms because of the complicated algebra.

Generally, since good theoretical procedures are lacking for intermediate-range forces, one is often forced to add the short-range forces to the long-range forces, and hope for the best.

3. Intermediate-Long-range forces

The part dealing with the attractive part of the potential is somewhat more difficult. Normally, one of several semi-empirical potential functions is assumed and the attempt is made to determine the parameters by successive approximations.[7]

Listed below are the equations for a number of the most frequently used empirical or semi-empirical inter-molecular potential functions:

Lennard-Jones $(n, 6)$ $\dfrac{V}{\varepsilon}=\dfrac{6}{n-6}\left(\dfrac{r}{r_m}\right)^{-n}-\dfrac{n}{n-6}\left(\dfrac{r}{r_m}\right)^{-6}$

typically n≅12, usually ranging from 8 to 20.

Buckingham Exp $(\alpha, 6)$ $\dfrac{V}{\varepsilon}=\dfrac{6}{\alpha-6}e^{-\alpha\left(\frac{r}{r_m}-1\right)}-\dfrac{\alpha}{\alpha-6}\left(\dfrac{r}{r_m}\right)^{-6}$

typically $\alpha\cong 12$, usually ranging from 8 to 20.

Kihara $(\gamma, 12, 6)$ $\dfrac{V}{\varepsilon}=\left(\dfrac{1-r}{r/r_m-\gamma}\right)^{12}-2\left(\dfrac{1-r}{r/r_m-\gamma}\right)^{6}$

typically r ≅ 0, usually ranging from−0.2 to 0.4

Morse (α) $\dfrac{V}{\varepsilon}=e^{-2\alpha\left(\frac{r}{r_m}-1\right)}-2\cdot e^{-\alpha\left(\frac{r}{r_m}-1\right)}$

typically $\alpha\cong 6$, usually ranging from 4 to 8.

Lennard-Jones (12, 6) potential function is the only realistic two parameter potential (ε,r_m or ε,σ) having been widely used.

In view of the difficulty in directly establishing the functional form of the potential from the scattering measurements, most authors have selected one or another of the conventional 3-parameter functionalities. In the absence of much detailed data, it has been customary to employ the simple 2-parameter Lennard-Jones (12, 6) potential.

4. Short-range forces

The physical origin of short range forces is clear enough, but detailed calculations usually have been either inaccurate or too complicated to be generally helpful. In the interaction of two atoms with closed electronic shells, the net effect is that the electronic clouds of the two atoms tend to avoid each other resulting in a repulsion between the atoms.

Short range forces appear in a first-order perturbation calculation.[8] The simplest function which might reasonably be expected is a singe exponential like $P(r)\exp(-ar)$ where $P(r)$ is a relatively slowly varying function of r. The most successful model for short- range forces is one which is applicable at such high energies that the detailed electronic structure of the atoms is un-important, namely a screened Coulomb function. The exponential form of repulsion $V(r) = P(r)\exp(-ar)$ is still a better representation of the potential within an accuracy of ca. 10% than the form of inverse power repulsions $V(r) = ar^{-n}$ over limited ranges of r.

6. Correlation ——

The elastic scattering behavior of atoms and molecules is completely determined by their interaction potential. We know that macroscopic studies influenced by intermolecular forces might be used to determine the forces. The most useful bulk properties for the study of intermolecular forces have been the equation of state, the transport coefficients of low-density gases, and a few crystal properties. Mathematically, one may regard the detailed form of the potential as having been mapped onto some macroscopic property. In practice, the potential cannot be reconstructed uniquely from that property alone; in many cases such a reconstruction is impossible even in principle.

All efforts made in choosing the model have to be absorbed into the numerical values of the adjustable constants. Caution is therefore necessary in giving any absolute interpretation to such numerical values. For instance, the coefficient of the r^{-6} term of a Lennard-Jones (12, 6) potential as determined from the second virial coefficient $B(T)$, is certainly not the true value of the London coefficient. In fact, it is too large by a factor of 2. The use of a more flexible model shows that this discrepancy is not real, but is only a symptom of over-simplification in the model.

The non-negligible dependence of the derived potential parameters upon the assumed functionality of the potential, along with the different sensitivity of the various measurements to different parts of the potential, and the wide variation in the parameters' values reported for the same system, makes the construction of a summary table of "experimental potentials" impossible. In other words, the wide variation in the parameter values reported for the same systsm depends on the type of measurement used and the experimenter's preference for a particular method of data analysis and curve fitting of results.

For the great majority of systems studied only a single potential parameter, namely the long-range C_6 coefficient, has been evaluated.

No potential function yet proposed is able to describe both the transport and second virial coefficients of even the inert gases within estimated experimental errors, even when several

adjustable constants are available. This affirms the conclusion that transport and virial coefficients cannot by themselves determine potential, but can act as important tests for the acceptance or rejection of proposed potentials.

Very few unambiguous and complete potential curves have emerged to date. It has been increasingly evident that potentials such as the 12-6, exp-6, kihara core, etc., are only good semi-quantitative models that must not be taken too literally, or over-seriously. Analysis of experimental data depends heavily on theory to suggest the form of the potential model.

The problem of rigorous "inversion" of experimental cross section data to yield the potential still remains to be solvel, even for a spherically symmetrical (or orientation averaged) potential refering to a single ground electronic state of the system. It appears that the principal contribution of most of these studies has been to spur the development of the experimental technique and to advance the methodology of data analysis.[9]

7. Bibliography ——

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