

NOTE 3

Quantum Nature of Intermolecular Interactions

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1 Long-range Intermolecular Interactions

Our goal is the calculation of the intermolecular interaction energy E between two molecules A and B ,

$$E = E(A \cdots B) - E(A) - E(B), \quad (1)$$

where $E(A)$ and $E(B)$ is the energy of each isolated molecule, respectively. After solving the Schrödinger equation

$$\hat{H}\Psi = E\Psi, \quad (2)$$

quantum mechanics provides both energy and quantum states describing the interacting molecular system.

Hamiltonian \hat{H} is represented as the sum of the Hamiltonians corresponding to the isolated molecules, $\hat{H}(A)$ and $\hat{H}(B)$ respectively, and the operator \hat{V} of the interaction between these molecules

$$\hat{H} = \hat{H}(A) + \hat{H}(B) + \hat{V} = \hat{H}^0 + \hat{V}, \quad (3)$$

where

$$\begin{aligned} \hat{H}(A) = & -\frac{1}{2} \sum_{a=1}^{N_A} \frac{1}{M_a^A} \nabla_a^2(A) - \frac{1}{2} \sum_{i=1}^{n_A} \nabla_i^2(A) - \sum_{a=1}^{N_A} \sum_{i=1}^{n_A} \frac{Z_a^A}{|\mathbf{R}_a^A - \mathbf{r}_i^A|} \\ & + \sum_{a=1}^{N_A} \sum_{b>a}^{N_A} \frac{Z_a^A Z_b^A}{|\mathbf{R}_a^A - \mathbf{R}_b^A|} + \sum_{i=1}^{n_A} \sum_{j>i}^{n_A} \frac{1}{|\mathbf{r}_i^A - \mathbf{r}_j^A|}, \end{aligned} \quad (4)$$

$$\begin{aligned} \hat{H}(B) = & -\frac{1}{2} \sum_{a=1}^{N_B} \frac{1}{M_a^B} \nabla_a^2(B) - \frac{1}{2} \sum_{i=1}^{n_B} \nabla_i^2(B) - \sum_{a=1}^{N_B} \sum_{i=1}^{n_B} \frac{Z_a^B}{|\mathbf{R}_a^B - \mathbf{r}_i^B|} \\ & + \sum_{a=1}^{N_B} \sum_{b>a}^{N_B} \frac{Z_a^B Z_b^B}{|\mathbf{R}_a^B - \mathbf{R}_b^B|} + \sum_{i=1}^{n_B} \sum_{j>i}^{n_B} \frac{1}{|\mathbf{r}_i^B - \mathbf{r}_j^B|}, \end{aligned} \quad (5)$$

and

$$\hat{V} = - \sum_{a=1}^{N_A} \sum_{i=1}^{n_B} \frac{Z_a^A}{|\mathbf{R}_a^A - \mathbf{r}_i^B|} - \sum_{a=1}^{N_B} \sum_{i=1}^{n_A} \frac{Z_a^B}{|\mathbf{R}_a^B - \mathbf{r}_i^A|} + \sum_{i=1}^{n_A} \sum_{j=1}^{n_B} \frac{1}{|\mathbf{r}_i^A - \mathbf{r}_j^B|} + \sum_{a=1}^{N_A} \sum_{b=1}^{N_B} \frac{Z_a^A Z_b^B}{|\mathbf{R}_a^A - \mathbf{R}_b^B|}. \quad (6)$$

At large distances, the operator \hat{V} may be treated as a small perturbation. Neglecting the electron exchange, the zeroth-order wave functions can be approximated as a simple product of the wave functions of isolated molecules:

$$\hat{H}^0 \Psi_n^A \Psi_m^B = (E_n^A + E_m^B) \Psi_n^A \Psi_m^B. \quad (7)$$

Then, a perturbative approach can be applied to study the long-range interaction between two molecules.

1.1 Electrostatic Intermolecular Interactions

Applying perturbation theory, the first-order correction to the energy of isolated molecules is equal to the expectation value of the perturbation operator averaged over the zeroth-order wave:

$$E^{(1)} = \langle \Psi_n^A \Psi_m^B | \hat{V} | \Psi_n^A \Psi_m^B \rangle \quad (8)$$

Equation (8) may be expressed in terms of the electron density because in quantum mechanics, instead of the point charges of classical mechanics, the charges are distributed in space with the probability density determined by $|\Psi(r, R)|^2$. In the adiabatic approximation, the set of nuclear coordinates R is fixed and the nuclei are considered as point charges. The electron charge is distributed in space with the one-electron density defined as:

$$\rho_{nn}^A(i) = N_A \int |\Psi_n^A(1, \dots, i, \dots, N_A)|^2 dV^{(i)}, \quad (9)$$

$$\rho_{mm}^B(j) = N_B \int |\Psi_m^B(1, \dots, j, \dots, N_B)|^2 dV^{(j)}, \quad (10)$$

for molecules A and B, respectively. Numbers in Eq. (9) and Eq. (10) denote the electron coordinates of enumerated electrons; $dV^{(i)}$ is an elementary volume of the configuration space of all electrons, belonging to molecule A, with the exception of the i th electron. The integration includes the summation over the whole spin space. The pre-integral factors are required for the conservation of electric charge, since the integration of ρ_{nn}^A over the configuration space of the i th electron must give the total number of electrons belonging to molecule A.

Substituting (6) into Equation (8) and taking into account the definition of the electron density, the following expression for the interaction of two molecules is obtained:

$$\begin{aligned} E^{(1)} = & - \sum_{a=1}^{N_A} Z_a^A \int \frac{\rho_{mm}^B(j)}{|\mathbf{R}_a^A - \mathbf{r}_j^B|} dV^{(j)} - \sum_{a=1}^{N_B} Z_a^B \int \frac{\rho_{nn}^A(i)}{|\mathbf{R}_b^B - \mathbf{r}_i^A|} dV^{(i)} \\ & + \sum_{i=1}^{n_A} \sum_{j=1}^{n_B} \frac{\rho_{nn}^A(i) \rho_{mm}^B(j)}{|\mathbf{r}_i^A - \mathbf{r}_j^B|} dV^{(i)} dV^{(j)} + \sum_{a=1}^{N_A} \sum_{b=1}^{N_B} \frac{Z_a^A Z_b^B}{|\mathbf{R}_a^A - \mathbf{R}_b^B|}. \end{aligned} \quad (11)$$

Clearly, the above expression for $E^{(1)}$ can be interpreted as a classical electrostatic energy for space distributed electron charges and point nuclear charges. The first two terms correspond to the energy of attraction between the nuclei of one molecule and the electron charge distribution of the other. The third and fourth terms represent the repulsion energy of the electron charge distributions and the nuclear charges, respectively.

With large distances between molecules, charge distributions do not overlap. Then, the electrostatic energy may be represented with good accuracy as a sum of a few terms of an expansion series

for $E^{(1)}$ in powers of $1/R$. Such an expansion series is based on the concept of the multipole moments of the charge distribution (see multipole expansion in Appendix on Electrostatic). In the case of two dipolar axially symmetric molecules in the configuration of Figure 3.1, the electrostatic term reads

$$u_{elec} = E^{(1)} = u(\mu, \mu) + u(\mu, \Theta) + u(\Theta, \Theta), \quad (12)$$

where

$$u(\mu, \mu) = \frac{\mu_1 \mu_2}{R^3} (2 \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \phi), \quad (13)$$

$$u(\mu, \Theta) = \frac{3}{2} \frac{\mu_1 \Theta_2}{R^4} [\cos \theta_1 (3 \cos^2 \theta_2 - 1) + 2 \sin \theta_1 \sin \theta_2 \cos \theta_2 \cos \phi] + \frac{3}{2} \frac{\mu_2 \Theta_1}{R^4} [\cos \theta_2 (3 \cos^2 \theta_1 - 1) + 2 \sin \theta_1 \cos \theta_1 \sin \theta_2 \cos \phi], \quad (14)$$

$$u(\Theta, \Theta) = \frac{3}{4} \frac{\Theta_1 \Theta_2}{R^5} (1 - 5 \cos^2 \theta_1 - 5 \cos^2 \theta_2 + 17 \cos^2 \theta_1 \cos^2 \theta_2 + 2 \sin^2 \theta_1 \sin^2 \theta_2 \cos^2 \phi + 16 \sin \theta_1 \sin \theta_2 \cos \theta_2 \cos \phi), \quad (15)$$

with $\phi = \phi_1 - \phi_2$.

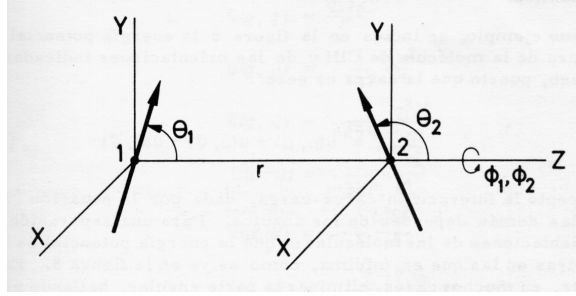


Figure 3.1: The coordinates describing the configuration of two axially symmetric molecules.

1.2 Induction Intermolecular Interactions

The calculation of the second order term of the Rayleigh-Schrödinger perturbation theory generates the expression for the energy of interaction between two molecules in their ground states:

$$E^{(2)} = - \sum_{n \neq m} \frac{|\langle \Psi_n^A \Psi_m^B | \hat{V} | \Psi_0^A \Psi_0^B \rangle|^2}{(E_n^A - E_0^A) + (E_m^B - E_0^B)}. \quad (16)$$

That contribution is termed the *polarization interactions*. The summation over n and m may be divided into two parts separately. The first part

$$E_{ind}^{(2)} = - \sum_{m \neq 0} \frac{|\langle \Psi_0^A \Psi_m^B | \hat{V} | \Psi_0^A \Psi_0^B \rangle|^2}{(E_m^B - E_0^B)} - \sum_{n \neq 0} \frac{|\langle \Psi_n^A \Psi_0^B | \hat{V} | \Psi_0^A \Psi_0^B \rangle|^2}{(E_n^A - E_0^A)} \quad (17)$$

is termed the *induction energy*. The first term in (17) describes the electrostatic interaction of molecule A, characterized by the ground state electron density, $\rho_{00}^A(i)$ with molecule B, characterized by an

induced transition electron density $\rho_{m0}^B(j)$. Similarly, the second term in (17) corresponds to the interaction of molecule B in its ground state with the induced electron density distribution of molecule A.

In the case of two dipolar axially symmetric molecules in the configuration of Figure 3.1, the induction term reads

$$u_{ind} = u(\mu, \alpha) + u(\mu\Theta, \alpha) + u(\Theta, \alpha)$$

where

$$u(\mu, \alpha) = -\frac{1}{2R^6} [\mu_1^2\alpha_2(3\cos^2\theta_1 - 1) + \mu_2^2\alpha_1(3\cos^2\theta_2 - 1)], \quad (18)$$

$$u(\mu\Theta, \alpha) = -\frac{12}{R^7} (\mu_1\Theta_1\alpha_2\cos^3\theta_1 + \mu_2\Theta_2\alpha_1\cos^3\theta_2), \quad (19)$$

$$u(\Theta, \alpha) = -\frac{9}{8R^8} [\Theta_1^2\alpha_2(\sin^4\theta_1 + 4\cos^4\theta_1) + \Theta_2^2\alpha_1(\sin^4\theta_2 + 4\cos^4\theta_2)], \quad (20)$$

with

$$\alpha = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp}),$$

the subscripts \parallel and \perp denote component along and at right angles to the axis of symmetry.

2 Dispersion Intermolecular Interactions

The rest part of Eq. (16) after subtracting $E_{ind}^{(2)}$ is the dispersion interaction:

$$E_{disp}^{(2)} = - \sum_{m,n \neq 0} \frac{|\langle \Psi_n^A \Psi_m^B | \hat{V} | \Psi_0^A \Psi_0^B \rangle|^2}{(E_n^A - E_0^A) + (E_m^B - E_0^B)}. \quad (21)$$

The matrix elements on the above term correspond to the electrostatic interaction of two mutually induced electron distributions. The dispersion energy is determined by the quantum-mechanical fluctuations of the electron density. Fluctuations cause the redistribution of the electron density in atoms and molecules. An instantaneous charge distribution, corresponding to an instantaneous dipole (and higher-order multipoles) moment of one molecule, induces a multipole moment on the other. The interaction of these moments defines the dispersion energy. For molecules in their ground states, it is always negative, that is, it corresponds to an attraction. The attractive dispersion forces are often called the van der Waals forces.

The multipole expansion for dispersion energy is usually written as a series with coefficients C_n denoted as dispersion coefficients

$$E_{disp}^{(2)} = - \sum_{n=6}^{\infty} \frac{C_n}{R^n}. \quad (22)$$

For interaction between atoms, the above series contains only even powers of n .

3 Short-range Intermolecular Interactions

At short distances the interaction energy has a repulsive nature and the electronic exchange, due to the overlap of the molecular electronic shells, dominates. The origin of the exchange interaction is in the Pauli principle. According to the latter, the wave function of a many-electron system must be antisymmetric with respect to permutations of electrons. This leads to some new terms in the expression of the electrostatic energy that do not appear in the previous approach for the direct electrostatic interaction. Thus, it is a specific quantum-mechanical effect. In the classical limit, the exchange interaction is turned to zero.

A good approximation to describe the short-range intermolecular interaction energy is the Born-Mayer potential

$$E(R) = A \exp(-bR), \quad (23)$$

where A and b are characteristic constant of each system. Taking logarithm on both sides in Eq. (23)

$$\ln E = \ln A - bR, \quad (24)$$

and derivation with respect to R

$$\frac{d \ln E}{dR} = -b, \quad (25)$$

$$\frac{d \ln E}{dR} R = -bR, \quad (26)$$

we obtain

$$\frac{d \ln E}{d \ln R} = -bR \quad (27)$$

It is noteworthy energy increase steeply in a short interval of R . So, in that interval

$$\frac{d \ln E}{d \ln R} \approx -n \quad (28)$$

where n is a constant. Therefore, by integration

$$\ln E \approx -n \ln R + \ln K, \quad (29)$$

i.e.,

$$E \approx \frac{K}{R^n}. \quad (30)$$

Reasonable results are obtained with $n = 12$.

Problems

3.1 Plot the interatomic interaction energy for rare gas from He to Rn using the model reported by Tang and Toennies in J. Chem. Phys. 118 (2003) 4976-4983 [DOI: 10.1063/1.1543944]

$$E(R) = Ae^{-bR} - \sum_{n=3}^N f_{2n}(bR) \frac{C_{2n}}{R^{2n}},$$

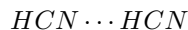
where

System	R_m	$\varepsilon \times 10^4$	C_6	C_8	C_{10}	A	b
$He \cdots He$	5.62	0.348	1.461	14.11	183.6	41.96	2.523
$Ne \cdots Ne$	5.84	1.34	6.383	90.34	1536	199.5	2.458
$Ar \cdots Ar$	7.10	4.54	64.30	1623	49060	748.3	2.031
$Kr \cdots Kr$	7.58	6.38	129.6	4187	155500	832.4	1.865
$Xe \cdots Xe$	8.25	8.96	285.9	12810	619800	951.8	1.681
$Rn \cdots Rn$	8.46	12.6	420.6	19260	1067000	5565	1.824

3.2 Los aspectos fundamentales de las llamadas fuerzas de van der Waals, pueden ser entendidos usando un modelo monodimensional formado por dos átomos que contienen electrones enlazados a los núcleos mediante fuerzas tipo oscilador armónico. Siguiendo la sección II del artículo: B.R. Holstein, *Am. J. Phys.* **69**, 441 (2001), deduzca la dependencia $\sim R^{-6}$ de este tipo de fuerzas.

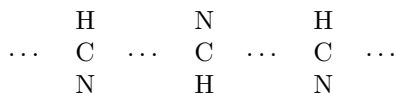
3.3 Al estudiar las moléculas de HCN tanto en fase gas como en fase cristalina se han encontrado los siguientes hechos experimentales:

(a) En fase gas se forman dímeros lineales del tipo



[Ref.: A.C. Legon, D.J. Millen, P.J. Mjöberg, *Chem. Phys. Lett.* **47**(1977)589-591]

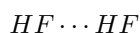
(b) En cambio, en fase sólida, el HCN cristaliza en cadenas del tipo



[Ref.: W.J. Dulmage, W.N. Lipscomb, *Acta. Cryst.* **4** (1951)330-334]

¿Cómo explica ambos hechos experimentales en términos de las interacciones intermoleculares?

3.4 Un interesante ejemplo de sistemas químicos en que las fuerzas intermoleculares son esenciales, son las llamadas *moléculas van der Waals*. Una molécula van der Waals es un complejo formado en fase gas entre dos monómeros estables neutros. En 1983, Buckingham y Fowler formularon un modelo muy simple y útil para predecir la geometría en equilibrio de moléculas van der Waals. Este modelo se basa en las interacciones electrostáticas asociadas a la expansión multipolar (carga efectiva atómica, momento dipolar, momento cuadrupolar, etc.). Usando el modelo Buckingham-Fowler prediga la geometría de las siguientes especies en fase gas:



[Ref.: A.D. Buckingham and P.W. Fowler, *J. Chem. Phys.* **19**, 6426 (1983)]