ESTIMATES OF GEOMETRY OF MOLECULAR COMPLEXES BASED ON ANALYSIS OF INTERMOLECULAR FORCES*

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Expressions are given for the Coulomb, dispersion, induction, charge-transfer, and exchange-repulsion energies that permit a simple estimation of the overall interaction energy. The procedure is applied to several configurations of the $(N_2)_2$, $(CO)_2$, and $C_2H_4 + Cl_2$ complexes.

Determination of the structure of a weak complex of two molecules represents an important task in both experimental and theoretical chemistry. Complexes of this type form a link between the free reactants and the activated complex on the reaction path which is one of the main reasons why they are of interest to chemists. Until recently experimentalists were able only to demonstrate the mere presence of weak complexes; the determination of their structure was too difficult a task. Some information (though not complete) about the structure has been obtained only recently from advanced spectroscopic experiments[1,2]. Theoretical approaches on different levels of sophistication are still far from being able to give safe predictions of the structure of weak complexes. The only exception is the family of complexes of strongly polar molecules whose geometries are predicted correctly by nonempirical and semiempirical calculations[3]. The situation with regard to the complexes of nonpolar molecules can be characterized by the example of as simple a complex as $(H_2)_2$. Here even the *ab initio* SCF CI calculations[4,5] are incapable of giving an unambiguous prediction of the order of $(H_2)_2$ structures. Since the use of advanced methods is associated with the considerable cost, it is topical to look for procedures that would provide qualitative geometry estimates of simple molecular complexes without the use of computers.

In this paper we have analyzed the terms for the Coulomb, dispersion, induction, charge-transfer and exchange-repulsion energies. We attempted to give them expressions which would permit an estimation of the relative stabilities of various configurations of diatomic as well as of some other simple molecules. A study of this type has not been undertaken so far. The only data available in the literature are the components of the total interaction energy tabulated for a particular pair of molecules in different mutual orientations[6].

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*   Part VI in the series Weak Intermolecular Interactions; Part V: This Journal *40*, 809 (1975).

RESULTS AND DISCUSSION

Table I presents contributions to the total interaction energy and, moreover, qualitative data on the magnitude of the overlap of the frontier orbitals ($+$ and 0 mean effective (positive) and ineffective (vanishing) overlaps, resp.) in certain configurations of donor–acceptor complexes of various types. In the following paragraphs the interaction energy components and the exchange repulsion energy will be discussed in more detail and the limits of applicability of the expressions given in Table I will be ascertained.

Coulomb energy. The expressions for the dipole–dipole $(E_{\mu-\mu}^C)$ and quadrupole–quadrupole (E_{Q-Q}^C) interactions are as follows[6]:

$$E_{\mu-\mu}^C = \frac{\mu_R \mu_T}{r^3} \left[\sin \Theta_R \sin \Theta_T \cos (\Phi_R - \Phi_T) - 2 \cos \Theta_R \cos \Theta_T\right], \qquad (1)$$

$$E_{Q-Q}^C = \frac{3 Q_R Q_T}{16 r^5} \{1 - 5 \cos^2 \Theta_R - 5 \cos^2 \Theta_T - 15 \cos^2 \Theta_R \cos^2 \Theta_T +$$

$$+ 2[\sin \Theta_R \sin \Theta_T \cos (\Phi_R - \Phi_T) - 4 \cos \Theta_R \cos \Theta_T]^2\}, \qquad (2)$$

where μ and Q denote the respective dipole and quadrupole* moments, and where r s the distance between the centers of the two systems. The geometry data and the mutual orientation of the systems R and T are outlined in Fig. 1 and Table I. The expressions for the energy components given in Table I do not hold in general. In the case of the dipole–dipole interaction their use is restricted to diatomic molecules (HF, HCl) and to polyatomic molecules in which the dipole moment is due to a particular group of atoms (*e.g.* a bond). With quadrupole–quadrupole interactions, the validity of the formulas is limited to a molecule of the cylindrical symmetry (*e.g.* the linear molecules H_2, N_2, C_2H_2).

Induction energy. The induction energy[6] was evaluated by means of the following formula

$$E^I = -\tfrac{1}{2} r^{-6} \mu_T^2 \alpha_R (3 \cos^2 \Theta_R + 1), \qquad (3)$$

where μ and α are the electric dipole moment and the polarizability respectively. Geometries assumed are specified in Table I. The expression (3) can be applied to interactions of a dipole T with an uncharged spherically symmetric molecule R. Conclusions drawn in Table I can be applied to diatomic dipoles or to polyatomic molecules in which a certain group of atoms gives a prevailing contribution to the

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* The tensor of the molecular quadrupole moment can be specified by a scalar Q provided the molecule is of cylindrical symmetry.

TABLE I

Expressions for Coulomb (E^C), Induction (E^I), and Dispersion (E^D) Energies, and Overlaps of Frontier Orbitals, S, for Various Mutual Orientations of Molecules R and T

	Configuration[a]		E^{C}[b]		E^I	E^D	S			
	R	T	$\mu-\mu$	$Q-Q$			$\pi-\pi^*$	$\pi-\sigma^*$	$\sigma-\sigma^*$	$\sigma^*-\pi^*$
1.	→	→	$-\dfrac{2\mu_R\mu_T}{r^3}$	$\dfrac{24}{16}\dfrac{Q_RQ_T}{r^5}$	$-\dfrac{8}{4}\dfrac{\mu_T^2\alpha_R}{r^6}$	$C_1(C_2 + 4C_3 + 4C_4 + 4C_5)$	$+$	0	$+$	0
2.	→	↗	$-\dfrac{\mu_R\mu_T}{r^3}$	$\dfrac{3}{16}\dfrac{Q_RQ_T}{r^5}$	$-\dfrac{5}{4}\dfrac{\mu_T^2\alpha_R}{r^6}$	$C_1(C_2 + \tfrac{5}{2}C_3 + 4C_4 + 2C_5)$				
3.	→	←	0	$-\dfrac{12}{16}\dfrac{Q_RQ_T}{r^5}$	$-\dfrac{2}{4}\dfrac{\mu_T^2\alpha_R}{r^6}$	$C_1(C_2 + C_3 + 4C_4)$	$+$	$+$	$+$	0
4.	→	↙	$\dfrac{\mu_R\mu_T}{r^3}$	$-\dfrac{3}{16}\dfrac{Q_RQ_T}{r^5}$	$-\dfrac{5}{4}\dfrac{\mu_T^2\alpha_R}{r^6}$	$C_1(C_2 + \tfrac{3}{2}C_3 + 4C_4 + 2C_4)$	$+$		$+$	
5.	→	↓	$\dfrac{2\mu_R\mu_T}{r^3}$	$\dfrac{24}{16}\dfrac{Q_RQ_T}{r^5}$	$-\dfrac{8}{4}\dfrac{\mu_T^2\alpha_R}{r^6}$	$C_1(C_2 + 4C_3 + 4C_4 + 4C_5)$	$+$	0	$+$	0
6.	←	←	$\dfrac{\mu_R\mu_T}{r^3}$	$\dfrac{9}{16}\dfrac{Q_RQ_T}{r^5}$	—	$C_1(C_2 + C_3 + C_4 + C_5)$	0	0	0	
7.	←	→	$-\dfrac{\mu_R\mu_T}{r^3}$	$\dfrac{9}{16}\dfrac{Q_RQ_T}{r^5}$	—	$C_1(C_2 + C_3 + C_4 + C_5)$	0	0	0	
8.	|----	╱	0	$\dfrac{3}{16}\dfrac{Q_RQ_T}{r^5}$	—	$C_1(C_2 + C_3 + C_4)$	0	0^c	0	0

[a] The angle between the molecular axes in complexes 2 and 4 is 45° and 135°, respectively. [b] μ and Q stand for dipole and quadrupole moments. [c] This holds in case that the angle between the molecular axes is 90°; if the angle is 270° the overlap is nonvanishing.

total molecular dipole moment. Since the system R is spherically symmetric, we assumed only the configurations $1-5$.

Dispersion energy. The original London formula[7] for the dispersion energy is not suitable for our purposes because it was derived for systems with isotropic polarizability, *i.e.*, for systems of spherical symmetry, *e.g.*, atoms. In this paper we adopted the expression which makes use of bond polarizabilities[8]. Since our goal is to predict the order of stabilities of individual structures, all constants (*e.g.*, ionization potential, polarizability) referring to systems R and T were introduced into constants $C_1 - C_5$. This gives Eq. (4) which holds only for two bonds (one in R, the other in T):

$$E^D = C_1\{C_2 + C_3(3\cos^2 \Theta_R + 1) + C_4(3\cos^2 \Theta_T + 1) +$$
$$+ C_5[2\cos \Theta_R \cos \Theta_T - \sin \Theta_R \sin \Theta_T + \cos \Phi_R \cos \Phi_T]\}, \qquad (4)$$

where

$$C_1 = \frac{I(R) \cdot I(T)}{4r^6[I(R) + I(T)]}, \quad C_2 = 6\alpha_R^t \alpha_T^t, \quad C_3 = \alpha_R^t \delta_T,$$

$$C_4 = \alpha_T^t \delta_R, \quad C_5 = \delta_R \delta_T,$$

C_1 is negative, $C_2 - C_5$ are positive, $I(R)$ and $I(T)$ mean ionization potentials of systems R and T; α_R^t and α_R^l are the transversal and longitudinal polarizabilities of the bond in R, δ_R, and δ_T being the respective difference. The data on the geometry are given in Table I. As stated above Eq. (4) holds only for two bonds, though the expressions of Table I can also be applied to polyatomic molecules if the polarizability of a particular bond is dominant (the C—N, C—C, and C—O bond in HCN, C_2H_4, and H_2CO, resp.).

In the case of Coulomb and induction energies, Table I permits the direct prediction of the order of stabilities of individual structures. With the disperison energy it is only possible to state that the most favoured configurations are 1 and 5, next 2 and 4, and the least stable configuration is 8. For the sake of illustration we present in Table II the data on the dispersion energy for several configurations of the $(N_2)_2$ complex $(r = 3 \cdot 10^{-10}$ m and $4 \cdot 10^{-10}$ m$)$. The entries of the table predict the stabilities of configurations to be in the order 1 and 5, 2 and 4, 3, 6, 7, 8. The respective differences are seen to be rather small in absolute value.

Charge-transfer energy. The following simple expression for the charge-transfer energy between a donor and acceptor was derived by Mulliken[9]

$$E^{CT} = -|CS_{mn}|^2/\Delta E(m \to n), \qquad (5)$$

where C is a constant, S_{mn} is the overlap integral between the frontier MOs m and

n (m being in the R system, n in the T system), and $\Delta E(m \to n)$ is the respective transition energy. If a complex of two systems stabilized by the charge-transfer energy is treated and if the order of stabilities of different configurations is to be ascertained, it is possible to consider merely the overlap between the orbitals m and n. Stability can be expected for those configurations of the complex where the overlap is nonvanishing. We considered the configurations $1-8$ with orbitals m and n of the π,σ; π^*, σ^*-types as outlined in Fig. 2.

Exchange-repulsion energy. Murrell, and coworkers[10] arrived at the expression for the exchange-repulsion energy by making use of the perturbation treatment. If in the interaction only two atoms are involved, it is possible to obtained reasonable values by means of the following simple relationship[10]

$$E^{ER} = \sum_a^R \sum_b^T cr^{-1} S_{ab}^2 .$$

(6)

The summations in (6) run over the AOs of the two atoms, c is a constant, S_{ab} is the overlap integral between orbitals a and b, and r is the interatomic distance. Eq. (6) has also been applied[11] to molecules, the summation extending over all AOs of individual molecules. The remaining problem is to evaluate the constant. This however can be disregarded if only qualitative estimates of E^{ER} are to be made for different configurations of a particular complex.

We now apply the above conclusions to several simple complexes.

1. *The* N_2—N_2 *complex.* Here the attraction is mainly due to the dispersion energy, and to a lesser extent, to the Coulomb (quadrupole–quadrupole) energy. The dispersion interaction favours the configurations 1 and 5; lesser stabilization is found with

TABLE II

Coulomb Quadrupole-Quadrupole (E^{Q-Q}), Dispersion (E^D), and Total Attraction ($E^T = E^{Q-Q} + E^D$) Energies (in kJ/mol) for Different Configurations of the $(N_2)_2$ Complex

Configuration[a]	$r = 3 . 10^{-10}$ m			$r = 4 . 10^{-10}$ m		
	E^{Q-Q}	E^D	E^T	E^{Q-Q}	E^D	E^T
1.	0·728	−6·933	−6·205	0·172	−2·469	−2·297
2.	−0·092	−5·962	−6·054	−0·021	−2·121	−2·142
3.	−0·364	−4·996	−5·360	−0·088	−1·778	−1·866
6.	0·272	−4·176	−3·904	0·063	−1·485	−1·423
8.	0·092	−3·950	−3·858	0·021	−1·406	−1·385

[a] The configurations are outlined in Table I.

2, 4, and 3. The quadrupole–quadrupole interaction favours the configurations 3, 2, 4 and destabilizes 1 and 5. The two energy contributions and their sums are entered in Table II for several configurations with $r = 3.10^{-10}$ m and $r = 4.10^{-10}$ m. In the calculation the following values[12,13] were used: $Q = 4.7 . 10^{-40}$ Cm; $\alpha_L = 2.38 . 10^{-30}$ m³; $\alpha_T = 1.45 . 10^{-30}$ m³; $I = 15.6$ eV $= 1505$ kJ. Table II shows that the dispersion energy is considerably lower than the Coulomb energy* in all configurations and, moreover, that the total attraction energies for the configurations 1, 2, and 3 are close in value. Apparently, the most stable one among them will be that which is the poorest in the exchange-repulsion energy. Let us examine the respective configurations for $r = 3 . 10^{-10}$ m. Assuming the constant c in (6) is independent of the interatomic distance, the exchange-repulsion energies for the configurations 1, 2, and 3 become $0.0452c$, $0.0194c$, and $0.0053c$, respectively.** Since c, which is always positive and which amounts (for $r = 3 . 10^{-10}$ m) approximately to $3300 . 10^{-10}$ mkJ/mol, the lowest exchange-repulsion energy is predicted for configuration 3. Configuration 3 is associated with the most negative total interaction energy and is therefore predicted to be the most stable. The $(N_2)_2$ complex was studied experimentally by Ewing[1]. From indirect evidence (both theoretical and experimental), the authors[1] concluded that the T shaped configuration of $(N_2)_2$ dimer is probable.

2. *The* CO—CO *complex.* The attraction energy is primarily due to the dispersion energy and only to a non-significant extent due to the dipole–dipole interaction energy. The dispersion energy term favours configurations 1 and 5. The values of the two energy terms and their sums are presented in Table III for several configurations with $r = 2 . 10^{-10}$ m and $r = 3 . 10^{-10}$ m. This relatively small value has been used in order to show that the Coulomb term is very small even at rather short distances. The calculations were based on the following values[14–16]: $\mu = 0.40 . 10^{-30}$ Cm; $\alpha_L = 2.6 . 10^{-30}$ m³, $\alpha_T = 1.62 . 10^{-30}$ m³, $I = 14.0$ eV $= 1351$ kJ. It is seen that the dispersion energy is two orders higher than the Coulomb energy in all configurations. The insignificant magnitude of the Coulomb energy is understandable with respect to the low dipole moment of the CO molecule. It should be noted that the dipole moments of polar molecules are considerably higher,[14] *e.g.* $\mu(HCl) = 3.67 . 10^{-30}$ Cm, $\mu(H_2O) = 6.15 . 10^{-30}$ Cm, $\mu(NaCl) = 28.39 . 10^{-30}$ Cm. Obviously, the dipole–dipole interaction energy in the pairs of HCl and NaCl molecules is much higher than it is in CO. For the sake of comparison we present its values (in kJ/mol)

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* It should be recalled that the quadrupole moment of the N_2 molecule is rather high compared to other molecules. For example in H_2, O_2, F_2, and CO_2 it is[12] 2.17, -1.3, 3.0, and $-14.4 . 10^{-40}$ Cm, resp.

** These values were given by calculations in which all AOs of the two systems were taken into account. By examination of overlaps of different pairs of AOs one finds that the squares of overlaps are close to zero unless the two orbitals are of the $2s$ and $2p_x$ types and are located on the nearest atoms of the two systems.

for the configurations 1, 2, 3, 6 and 8 of $(HCl)_2$ $(-5\cdot401, -2\cdot700, 0, 2\cdot700, 0)$ and $(NaCl)_2$ $(-322\cdot55, -161\cdot28, 0, 161\cdot28, 0)$ for $r = 3 \cdot 10^{-10}$ m.

3. C_2H_4—Cl_2 complex. With this complex no significant Coulomb energy can be expected. As in the foregoing cases, the dispersion energy favours the configurations 1 and 5, 2 and 4, and 3. Since the C_2H_4 molecule is a rather strong electron donor and Cl_2 a rather strong acceptor, a significant charge-transfer energy can be anticipated. The complex is of the π–σ^* type. A nonzero overlap between the HOMO in C_2H_4 and LFMO in Cl_2 is only found with configurations 3 and 8 (see footnote *b* in Table I). It should be emphasized that the conclusions about the dispersion and charge-transfer energy do not hold only for the configuration 3 (the two systems lie in the yz plane — *cf.* Fig. 1), but also for a complex of the same shape, where two molecules lie in perpendicular planes yz and yx (in the literature this shape is called axial). The C_2H_4—Cl_2 complex has recently been studied experimentally and theoretically by Nelander[17,18]; it was concluded that the structure is axial.

Up to now we were concerned with the estimates of the most stable structures of complexes formed by two diatomic (or polyatomic) molecules. Next we treat two other cases important for practical purposes — the complexes formed by an ion and a molecule or by an atom and a molecule.
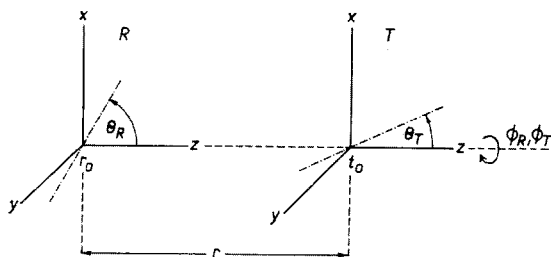

FIG. 1

Orientation of Molecules *R* and *T*

    Points r_0 and t_0 represent the geometrical centres of molecules *R* and *T*. The staggered lines passing through r_0 and t_0 are directions of dipoles and quadrupoles of cylindrically symmetric systems *R* and *T*. The angles Θ_T and Θ_R are situated in the xz-plane.
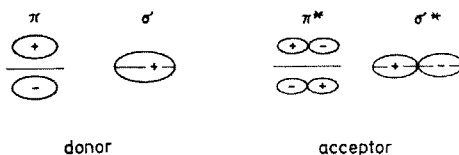

FIG. 2

Shapes of the Frontier Orbitals of the Electron Donor and Acceptor

The Interaction Ion–Molecule

Coulomb energy. In the multipole expansion[19] we restrict ourselves to the first two terms, *i.e.*, to the interactions of the charge of one system with the dipole and quadrupole of the other:

$$E^C = \frac{q\mu}{r^2} \cos \Theta + \frac{qQ}{r^3} \left(\tfrac{3}{2} \cos^2 \Theta - \tfrac{1}{2}\right). \tag{7}$$

Here q stands for the charge of the ion, the other symbols have the same meaning as in the preceding relationships (Fig. 1).

Induction energy. We restrict ourselves to the first term of the respective expansion[19]. This term corresponds to the interaction of the charge of one system with the induced charge of the other:

$$E^I = - \frac{q^2}{2r^4} \left[\alpha + \tfrac{1}{3}(\alpha_\| - \alpha_\perp)(3 \cos^2 \Theta - 1)\right]. \tag{8}$$

Here α, $\alpha_\|$, and $\alpha_\perp$ mean, respectively, the total polarizability and its components along and at the right angle to the axis of symmetry.

The dispersion term is disregarded in this case because it is negligible with respect to terms mentioned above.

The Interaction Atom–Molecule

Dispersion energy. This is given[19] by the following relationship

$$E^D = - \frac{3}{2} \frac{I_R I_T}{I_R + I_T} r^{-6} \left[\alpha_R \alpha_T + \tfrac{1}{3}\alpha_R(\alpha_\| - \alpha_\perp)_T \left(\tfrac{3}{2} \cos^2 \Theta - \tfrac{1}{2}\right)\right]. \tag{9}$$

If r is constant, it is possible to write

$$E^D = C_1 \left[C_2 + \tfrac{1}{3}C_3 \left(\tfrac{3}{2} \cos^2 \Theta - \tfrac{1}{2}\right)\right]. \tag{10}$$

For the constants C_1, C_2, and C_3 it holds $C_1 < 0$, $C_2 > 0$, $C_3 > 0$.

Induction energy. The truncation of the multipole expansion[19] to the very first term, which is due to the interaction of the dipole of one system with the induced dipole of the other, gives us

$$E^I = - \frac{\mu^2 \alpha}{2r^6} \left(3 \cos^2 \Theta + 1\right). \tag{11}$$

Table IV presents results for the linear and T shaped configurations: Coulomb and induction energies for the complex positive ion-molecule and dispersion and induction energies for the complex atom-molecule.

In the interaction ion-dipole both Coulomb and induction terms favour the linear structure $\left(\alpha_{\parallel}\right.$ is always higher than $\left.\alpha_{\perp}\right)$. In contrast, the interaction ion-quadrupole

<small>TABLE III</small>

Coulomb Dipole-Dipole $(E^C_{\mu-\mu})$, Dispersion (E^D), and Total Attraction $(E^T = E^C_{\mu-\mu} + E^D)$ Energies (in kJ/mol) for Different Configurations of the $(CO)_2$ Complex

Configuration[a]	$r = 2 \cdot 10^{-10}$ m			$r = 3 \cdot 10^{-10}$ m		
	$E^C_{\mu-\mu}$	E^D	E^T	$E^C_{\mu-\mu}$	E^D	E^T
1.	$-0\cdot218$	$-85\cdot182$	$-85\cdot400$	$-0\cdot063$	$-7\cdot477$	$-7\cdot540$
2.	$-0\cdot109$	$-73\cdot835$	$-73\cdot944$	$-0\cdot033$	$-6\cdot481$	$-6\cdot514$
3.	$0\cdot0$	$-62\cdot488$	$-62\cdot488$	$0\cdot0$	$-5\cdot485$	$-5\cdot485$
5.	$0\cdot218$	$-85\cdot182$	$-84\cdot964$	$0\cdot063$	$-7\cdot477$	$-7\cdot414$
6.	$0\cdot109$	$-52\cdot455$	$-52\cdot346$	$0\cdot033$	$-4\cdot607$	$-4\cdot573$
7.	$-0\cdot109$	$-52\cdot455$	$-52\cdot564$	$-0\cdot033$	$-4\cdot607$	$-4\cdot640$
8.	$0\cdot0$	$-49\cdot919$	$-49\cdot919$	$0\cdot0$	$-4\cdot381$	$-4\cdot381$

[a] The configurations are outlined in Table I.

<small>TABLE IV</small>

Expressions for Coulomb (E^C), Induction (E^I), and Dispersion (E^D) Energies for Linear and T-Shaped Configuration of Positive Ion-Molecule and Atom-Molecule Complexes

Configuration	Positive ion-molecule			Atom-molecule	
	E^C		E^I	E^D	E^I
	$q-\mu$	$q-Q$			
$\bullet \rightarrow$	$-\dfrac{q\mu}{r^2}$	$\dfrac{qQ}{r^3}$	$-\dfrac{q^2\alpha_{\parallel}}{2r^4}$	$C_1C_2 + \frac{1}{3}C_1C_3$	$-\dfrac{2\mu^2\alpha}{r^6}$
$\bullet \uparrow$	0	$-\dfrac{1}{2}\dfrac{qQ}{r^3}$	$-\dfrac{q^2\alpha_{\perp}}{2r^4}$	$C_1C_2 - \frac{1}{6}C_1C_3$	$-\dfrac{1}{2}\dfrac{\mu^2\alpha}{r^6}$
$\bullet \leftarrow$	$\dfrac{q\mu}{r^2}$	$\dfrac{qQ}{r^3}$	$-\dfrac{q^2\alpha_{\parallel}}{2r^4}$	$C_1C_2 + \frac{1}{3}C_1C_3$	$-\dfrac{2\mu^2\alpha}{r^6}$

favours the *T* shaped configuration. In the case of the interaction atom-molecule, the linear structure is favoured by both the dispersion term (recall that C_1 is always negative and C_2 and C_3 are always positive) and the induction term.

These qualitative considerations conform to the *ab initio* SCF and SCF-CI calculations. Kutzelnigg and coworkers[20] studied the $Li^+ + H_2$ interaction (ion-quadrupole). Their both SCF and SCF-CI calculations favour the *T* shaped configuration. Tsalpine and Kutzelnigg[21] studied the $He—H_2$ complex and demonstrated that the deepest potential well is due to the linear configuration.

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Translated by P. Čársky.