

Corrections and notes on  
**The Theory of Intermolecular Forces, 2nd edition**

by Anthony J. Stone (Oxford University Press, 2013)

Last updated on 30 May 2016.

## Corrections

p. 5, Table 1.2:

The signs of the exchange-induction and exchange-dispersion contributions should both be “+”.

p. 17, Table 2.2:

The quadrupole moment of CO<sub>2</sub> is negative in any unit, D Å and C m<sup>2</sup> as well as atomic units.

p. 60, below eqn (4.2.3):

In the third line below the equation, there is a missing factor of  $-\frac{1}{2}$ . It should read:

and the induction energy is  $-\frac{1}{2}q^2\alpha_{zz}^B/((4\pi\epsilon_0)^2z^4)$ .

Thanks to Toby Zeng for pointing this out.

p. 164, eqn 9.1.17: The sign of the r.h.s. is incorrect: the equation should read

$$\tilde{T}_{\alpha\beta}^{ab} = \frac{3f_i R_\alpha R_\beta - f_e R^2 \delta_{\alpha\beta}}{4\pi\epsilon_0 R^5}$$

p. 165, eqn 9.1.22:

In this equation  $\lambda$  should be replaced by  $a$  throughout.

## Notes

The theory of intermolecular forces is an active and fast-moving field of research, and some topics are already out of date. These are some notes reflecting some of the advances that have come to my notice since the second edition went to press. It is by no means a comprehensive update.

### Deformation energy (§1.1.2, p. 4)

An example of the importance of the deformation energy is given by the distortion/interaction procedure for analysing the activation energies of organic reactions (Ess and Houk, 2007, 2008). Here the activation energy is viewed as the sum of the energy needed to distort the reacting molecules into their geometries at the transition state, and the interaction energy between the distorted fragments. The method is useful for understanding the relative activation energies for different reaction pathways leading to different products. In this case the distortion energy is substantial — comparable in magnitude to the interaction energy between the fragments.

### Calculation of potential energy surfaces (§5.6, pp. 87–92)

An article by Czako *et al.* (2013) compares a number of abinitio methods for calculating potential energy surfaces and estimates the size of the errors of each.

### Basis set superposition error and counterpoise correction (§5.6.2, pp. 88–91)

The object of the counterpoise correction is to reduce the basis set error in the monomer calculation, with the intention of bringing it closer to the basis set error in the dimer calculation, which is assumed to be smaller. In this way the errors in the two calculations are expected to more nearly cancel. An article by Mentel and Baerends

(2014) investigates basis superposition errors in detail for some small diatomics, in particular Be<sub>2</sub>, and concludes that the basis set error is already smaller for the atoms in the monomer basis than for the dimer, so that treating them in the dimer basis reduces their basis set error further, and *increases* the difference between the errors for the dimer and the monomers. In other words, it makes matters worse rather than better.

### Charge transfer energies (§8.3.2, pp. 150–153)

A new approach to the calculation of charge-transfer energies has been proposed by Misquitta (2013). It is based on the idea that while induction is the response of one molecule to the electric field of its neighbours, without any movement of electrons between molecules, the charge transfer arises from tunnelling of electrons into regions of low potential energy in the neighbouring molecules, namely the regions around their nuclei. Accordingly charge-transfer can be turned off by the regularization procedure described in §6.3.2. In this approach, the total induction energy for molecule A in the presence of B is calculated as usual, and an induction energy without charge-transfer is obtained by calculating the induction energy of A while applying regularization to the nuclear potentials of B. This suppresses the deep potential wells for A electrons near B nuclei, and so suppresses the charge-transfer effect. The unperturbed electronic ground-state wavefunction of B is unchanged in this calculation; only the nuclear attraction is modified. The charge-transfer energy is then taken to be the difference between these two calculations.

### Halogen bonding (§8.5, p. 157)

Recent calculations have shown that although the binding is due predominantly to the electrostatic effects, the linearity of the structure can be attributed primarily to the non-spherical nature of the bonded halogen atom (Stone (2013)).

### Fragment methods (§12.2.5, p. 218)

A special issue of *Phys. Chem. Chem. Phys.* (2012, vol. **14**, No. 21) was devoted to fragment methods for calculating wavefunctions and properties of large systems. See Beran and Hirata (2012) for the editors' introduction.

## References

- Beran, G. J. O. and Hirata, S. (2012) 'Fragment and localized orbital methods in electronic structure theory,' *Phys. Chem. Chem. Phys.* **14**, 7559–7561, special issue.
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