Three-body Retarded Dispersion Potentials Involving Electric Octupole Coupling

Akbar Salam

Wake Forest University, US

Email of Presenting Author: salama@wfu.edu

Over the years attention has rightly been focused on the Casimir-Polder dispersion potential between a pair of atoms or molecules since this is the dominant term of the van der Waals energy shift between neutral nonpolar species in their ground electronic states. It has also long been known that agreement with experimental crystal energies of noble gas elements is vastly improved if non-pairwise additive corrections to the dispersion energy are included [1]. In recent efforts to improve the quality of global potential energy surfaces, especially when considering low energy collisions involving alkali metal atoms and dimers at ultracold temperatures [2], and interaction energies between rare gases [3], it has been necessary to account for many-body effects and higher (dipole (D), quadrupole (Q), octupole (O), …) multipole moment contributions. In this talk we consider the effect of including electric octupole coupling on retarded dispersion interactions between three molecules. Using the Craig-Power Hamiltonian [4] of molecular QED theory [5,6], the following dispersion potentials are calculated: DD-DD-DO, DD-DO-DO, DO-DO-DO, DD-DD-OO and DD-DO-OO. Interesting features are found on decomposing the octupole moment into its irreducible components of weights-1 and -3. For each of the interactions studied, the contribution containing octupole weight-1 dependent term is found to be a higher-order correction to the retarded triple dipole (DD-DD-DD) dispersion potential [7]. A similar feature was noted in the dispersion energy shift between an electric dipole polarisable molecule and an electric octupole polarisable one (DD-OO), where the weight-1 octupole dependent term was seen to be a higher-order correction to the Casimir-Polder potential [8]. For isotropic three-body energy shifts involving mixed DO polarisability, the weight-3 contribution vanishes in all of the cases considered, leaving a retarded potential dependent upon the octupole weight-1 term. Results are presented for equilateral triangle and collinear geometries, as well as for arbitrary arrangements of the three species [9-12]. Far-zone asymptotically limiting forms are also given.

References

[1] G. C. Maitland et al, Intermolecular Forces, Clarendon, 1981.
[2] M. J. Cvitas, P. Soldan and J. M. Hutson, Mol. Phys. 104, 23 (2006).
[3] L-Y. Tan, Z-C. Yan, T-Y. Shi, J. F. Babb and J. Mitroy, J. Chem. Phys. 136, 104104 (2012).
[4] D. P. Craig and E. A. Power, Int. J. Quant. Chem. 3, 903 (1969).
[5] D. P. Craig and T. Thirunamachandran, Molecular Quantum Electrodynamics, Dover, 1998.
[6] A. Salam, Molecular Quantum Electrodynamics, Wiley, 2010.
[7] M. R. Aub and S. Zienau, Proc. Roy. Soc. London A257, 464 (1960).
[8] A. Salam and T. Thirunamachandran, J. Chem. Phys. 104, 5094 (1996).
[9] A. Salam, J. Chem. Phys. 139, 244105 (2013).

[10] A. Salam, J. Chem. Phys. 140, 044111 (2014).
[11] J. Aldegunde and A. Salam, Mol. Phys. 113, 226 (2015). [12] A. Salam, unpublished results.