Long-range retardation of relativistic interatomic potentials

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According to the Casimir-Polder theory the long-range interaction potential between spherically symmetric atoms results from the exchange of transverse virtual photons and vanishes as R^{-7} with the interatomic distance R. This damping of the nonrelativistic, London R^{-6} decay is interpreted as a result of the retardation of the propagation of electromagnetic interactions. It is known that the leading relativistic correction to the London theory derived from Dirac-Coulomb-Breit Hamiltonian behaves as R^{-4} at large R. The leading QED correction decays even slower, as R^{-3}. It will be shown how this apparently contradictory results can be reconciled and how the relativistic and QED calculations of the interatomic potential can be corrected for retardation to recover the correct R^{-7} behavior of the interatomic potential [1].

It will also be shown that for the interaction of two helium-4 atoms the Casimir-Polder retardation damping of the nonrelativistic interaction increases the dimer size by 2.0 Å relative to the nonrelativistic value of 44.6 Å. This damping is accounted for by the inclusion of the Breit interaction and the leading QED (Araki-Sucher) contributions to the potential [2]. The remaining retardation effect, of the fourth- and higher order in the fine-structure constant, is practically negligible for the bound state, but is important for the equation of state and for some thermophysical properties of gaseous helium.

As two helium-4 atoms form a dimer with significant wave function amplitudes at distances $R > 100$ Å, i.e., in the region where the retardation switches the London R^{-6} decay of the potential to the R^{-7} form, it has been assumed in the literature that this switching is responsible for the observed 2.0 Å (4.5%) increase of the bond length $\langle R \rangle$. We show that $\langle R \rangle$ is, in fact, insensitive to the potential at $R > 20$ Å and its increase is due to the Breit and Araki-Sucher corrections computed by us from expressions valid at short R, i.e., beyond the validity range of the Casimir-Polder theory [3]. Computation of these corrections seamlessly connects the Casimir-Polder theory to distances relevant for properties of long molecules.

[1] Cencek, W., Przybytek, M., Komasa, J., Mehl, J., Jeziorski, B., Szalewicz, K *J. Chem. Phys.*,136:224303, 2012.

[2] Przybytek, M., Cencek, W., Komasa, J., Lach, G., Jeziorski, B., Szalewicz, K *Phys. Rev. Lett.*, 104:183003, 2010.

[3] Przybytek, M., Jeziorski, B., Cencek, W., Komasa, J., Mehl, J., Szalewicz, K *Phys. Rev. Lett.*, 108:183201, 2012.