Van der Waals dispersion coefficients within the all-electron mixed-basis TOMBO approach

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The van der Waals interaction act between neutral atoms (clusters). At short distance, where overlap of the electronic clouds is non-negligible, atoms repel and at distance where overlap is negligible, atoms are attracted by mutual polarization of their electronic clouds. There is a fundamental difference between these repulsive and attractive interactions. The description of the repulsive interactions is performed within the framework of quantum chemistry while the attractive or van der Waals interaction are described with the rules of the quantum electrodynamics. In the framework of the general theory of van der Waals forces[1], neutral atoms in vacuum with the electromagnetic field fluctuations, absorb and emit photons. By absorption of photons atoms are transferred into excited states. This can lead to the appearance of virtual multipole moments whose interactions determine the attractive van der Waals interaction.

We implement a linear-response theory within the time-dependent local density approximation (TDLDA) to study the true electron excitations of atoms (clusters). Frequency-dependent polarizabilities and van der Waals dispersion coefficients for atoms (clusters) have been calculated using Casida method. The analytical expressions for the coupling matrix **K** describing the interaction between virtual Kohn-Sham electron excitations have been obtained in the framework of the all-electron mixed-basis approach. This allows us to obtain Casida equations for finding the true excitation energies and the oscillator strengths. These quantities have been used to find polarizabilities and van der Waals dispersion coefficients. The set of programs for calculation of properties of atoms was developed. Calculations were performed to obtain the Van der Waals dispersion coefficients for hydrogen atom, H–H, hydrogen H_2–H_2, oxygen O_2–O_2 and water H_2O–H_2O molecules. Comparisons with the results obtained by other methods have been also performed.

[1] Dzyaloshinskii, I. D., E. M. Lifshitz, and L. P. Pitaevskii, 1961, Usp. Fiz. Nauk **73**, 381 (Sov. Phys. Usp. **4**, 153 (1961)

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