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Intermolecular Interactions in a Radiation Field via the Method of Induced Moments

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The application of an external electromagnetic field modifies the energy shift between a pair of interacting molecules [1]. This phenomenon is the origin of optical binding forces and optically induced nanoelectromechanical torques. Within the framework of molecular quantum electrodynamics [2], the field induced intermolecular interaction energy is commonly calculated using fourth order perturbation theory together with summation over ninety-six time-ordered diagrams [3]. For a pair of coupled neutral polarizable molecules subject to the action of an electric field, two distinct mechanisms are found to contribute to the energy shift. One is the dynamic mechanism, proportional to the product of the electric dipole polarizability of each species, arising from scattering of a real photon at different centres and exchange of a virtual photon between the pair. A finite amount of energy is transferred. The second contribution, termed the static mechanism, occurs when one or both species is polar. It is proportional to the product of the static electric dipole moment and the first hyperpolarizability of each molecule. It arises when absorption and emission of a real photon takes place at the same site with a single virtual photon again crossing between the pair. No energy is relayed in this mechanism. It is shown how the method of induced moments provides a simple alternative approach to the computation of the change in energy shift relative to perturbation theory techniques, correctly accounting for both mechanisms [4,5]. The picture is one in which an applied electric field induces multipole moments in the two molecules. These are coupled via the dipole-dipole interaction tensor to leading order, giving rise to a field induced interaction energy on taking the expectation value over the ground state of each molecule and the radiation field described by a state containing *N* photons.

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