

Nonlocal dielectric functions at the intramolecular level

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I. Definition of the nonlocal response function

A nonlocal dielectric function $\epsilon(\mathbf{r}, \mathbf{r}'; \omega)$ characterizes the screening of an applied potential $\phi_o(\mathbf{r}', \omega)$. The dielectric function acts as an integral kernel to give the effective potential $\phi_e(\mathbf{r}, \omega)$ at points within the molecule:

$$\phi_e(\mathbf{r}, \omega) = \epsilon_o \int d\mathbf{r}' \epsilon(\mathbf{r}, \mathbf{r}'; \omega)^{-1} \phi_o(\mathbf{r}', \omega)$$

Using quantum perturbation theory within linear response, we have related $\epsilon(\mathbf{r}, \mathbf{r}'; \omega)$ to the charge-density susceptibility $\chi(\mathbf{r}, \mathbf{r}'; \omega)$, which gives the change in charge density at point \mathbf{r} due to a delta-function perturbing potential of frequency ω , applied at \mathbf{r}' [1]. Because the molecular environment is inhomogeneous and anisotropic, the nonlocal response function that relates the dielectric displacement $\mathbf{D}(\mathbf{r}, \omega)$ to the Maxwell field $\mathbf{E}(\mathbf{r}', \omega)$ is distinct from $\epsilon(\mathbf{r}, \mathbf{r}'; \omega)$ [2].

II. Dielectric theory of intermolecular interactions

At first order, the interaction energy of a pair of molecules depends on the charge density of each of the molecules, when isolated. No dielectric screening is present in the interaction energy at this order. However, the forces on the nuclei contain dielectric screening effects, even at first order. This result follows from a relationship between the charge-density susceptibility and the derivative of the molecular charge density with respect to any of the nuclear coordinates [3].

The induction and dispersion energies of a molecule are determined by intermolecular screening of the intramolecular Coulomb interactions. In a cluster of three molecules, each molecule screens the interactions between the remaining two, with the dielectric function obtained by considering the response of a single molecule to an external perturbing potential [4]. This result leads to a treatment of a dielectric medium on the molecular level, in a form that can be integrated with continuum dielectric theory.

The dielectric theory for the induction and dispersion forces on nuclei shows that the forces depend on nonlinear susceptibilities, although the corresponding energies can be obtained within linear response.

Ab initio computations of $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ and $\epsilon(\mathbf{r}, \mathbf{r}'; \omega)$ have been carried out [5]. We find that $\epsilon(\mathbf{r}, \mathbf{r}'; \omega)$ is negative for some pairs of points within a molecule, even when the frequency ω is zero.

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[2] O. S. Jenkins and K. L. C. Hunt, *J. Mol. Struct.—Theochem* **633**, 145 (2003).

[3] K. L. C. Hunt, *J. Chem. Phys.* **90**, 4909 (1989).

[4] A Mandal and K. L. C. Hunt, *J. Chem. Phys.* **131**, 24303 (2009).

[5] X. Li, R. L. Jacobsen, and K. L. C. Hunt, to be published.