

CHEMISTRY 4021/8021
MIDTERM EXAM 2 — SPRING 2013 — KEY

Q1) What is "dispersion"? How do different modeling techniques—both classical and quantum mechanical—include (or fail to include) dispersion? What kinds of "mistakes" would you expect to make in molecular modeling if your model fails accurately to account for dispersion? (30 points)

Dispersion is the induced-dipole-induced-dipole interaction associated with correlated electronic motion (i.e., dynamic correlation). It is the largest contributing component of medium to long-range (van der Waals) molecular interactions that fall off as r^{-6} (the others being thermally averaged dipole-dipole interactions and dipole-induced-dipole interactions). Dispersion interactions may also be called "London interactions" or "London forces".

Classical force fields tend to include a specific non-electrostatic, non-bonded term, one component of which is designed to include dispersion (e.g., the "6" part of a 6-12 potential). Semiempirical NDDO models that include "corrections" to nuclear repulsion (like AM1 and PM3) effectively do the same, albeit with gaussian functions at molecular contact distances.

Hartree-Fock *cannot* predict dispersion because it is intrinsically associated with dynamical electron correlation. So, most HF interactions between neutral molecules are unrealistically repulsive. MP2 and other correlated post-HF models, on the other hand, are fine for dispersion, as they include the necessary correlation.

DFT functionals generally fail for dispersion because an exponentially decaying density (which is realistic) cannot be used in a functional in a fashion that gives r^{-6} behavior for attraction. So, like HF, *most* (the M06 series of functionals is an exception) modern functionals are too repulsive for intermolecular interactions. To address this, post hoc dispersion terms are often added, e.g., to make B3LYP-D from B3LYP a non-bonded term looking much like that in a force field is included.

The error one would make with a poor treatment of dispersion is to underestimate non-bonded attractive forces. Thus, for instance, the binding constant of a guest to a host would be predicted to be too small without including dispersion accurately.

Q2) Four categories of density functionals include 1) LDA, 2) GGA, 3) meta-GGA, and 4) hybrid functionals. Explain how these categories differ from one another in terms of the "form" of their constituent functionals. Offer at least one example where a particular modeling problem might motivate a preference for a functional from one category more than from any of the others. (40 points)

The Local Density Approximation (LDA) energy expression depends only on the magnitude of the electron density at a given position in space (not counting the Kohn-Sham kinetic energy, which is computed in the same way for all of the functionals). In Generalized Gradient Approximation (GGA) extends the energy expression to depend also on the reduced gradient of the density (i.e., its rate of change normalized relative to its magnitude) at a given position in space, thereby taking greater note of the difference between molecular densities and the uniform ones that characterize a uniform electron gas. The meta-GGA functionals go on to include second derivative of the density information; this can take various forms, with the so-called kinetic-energy density being the most computationally convenient. A hybrid functional replaces some density functional exchange with some (exact) Hartree-Fock exchange. The particular amount is typically controlled by an empirically selected parameter or set of parameters (where the other parameters may balance the amounts of local and GGA contributions as well, for example). [As noted in the answer to the prior problem, adding a post facto correction for dispersion can be done for all of these functionals.]

Generally, hybrid functionals do better for the calculation of transition-state structure energies relative to minima. Generally local functionals that do not include HF exchange do better for systems containing transition metals or other situations where narrow frontier orbital separations may lead to multideterminantal character. Generally, the more modern meta-GGA options offer improved accuracy through testing against larger databases. Generally, local functionals offer *much* faster optimization strategies through density fitting.

Q3) The following two terms (written using atomic units) appear in the energy expression that would be computed for many functionals. Explain generally what the terms are and show that they do indeed each have the same (energy) units. (30 points)

$$\frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \qquad -\frac{9}{8} \left(\frac{3}{\pi}\right)^{1/3} \int \rho^{4/3}(\mathbf{r}) d\mathbf{r}$$

The first term is the classical repulsion of an electron density with itself, running continuously over all pairwise interactions of points in space, divided by 2 to correct for double counting of (r_1, r_2) interactions and (r_2, r_1) interactions. The second term is the LDA exchange energy (specifically, that derived by Slater) depending only on the local density $\rho(\mathbf{r})$ at a given position in space.

The units on density are "per volume". If we use bohr, as the atomic unit of length (it doesn't matter what unit we pick, but it helps to have a name...), that makes the units of density bohr⁻³. Clearly the $|\mathbf{r}_1 - \mathbf{r}_2|^{-1}$ term in the first expression has units of bohr⁻¹, and integration over a volume element $d\mathbf{r}$ will deliver units of volume, or bohr³.

So, in the density-density repulsion term we have two densities, multiplying to bohr⁻⁶, two volume integrations cancelling this by multiplying by bohr⁶, and all that is left is the denominator distance operator having units of bohr⁻¹. For the exchange energy term, we have (bohr⁻³)^{4/3}, which gives bohr⁻⁴. Multiplying by the integrated volume element bohr³ leaves bohr⁻¹, thus illustrating the common units. These are the expected energy units for charge-charge interactions which, taking charge to be implicit, follow Coulomb's law $E = q_1 q_2 / r_{12}$ with units of inverse distance.