CHEMISTRY 4021/8021
MIDTERM EXAM 3 — KEY

Q1) What physical effects contribute to the free energy of solvation, i.e., the free energy change associated with moving a solute molecule from the gas phase to a liquid solution at a constant standard-state concentration (e.g., 1 M)? How do most modern continuum solvation models incorporate those different effects into a calculation? (30 points)

The various effects are cavitation, dispersion, bulk electrostatic effects (which include interactions between the permanent electrical moments of the solute and solvent molecules as well as electronic polarization of the solute and electric polarization of the medium). In addition, free energy effects associated with changes in solvent structure in response to the solute can occur (e.g., the hydrophobic effect).

A reaction field is generated in the continuum by the charge distribution of the solute. In a classical model, that would lead to a simple electrostatic interaction. In a quantum mechanical model, the reaction field becomes a potential operator in the electronic Hamiltonian, and the reaction field is determined self-consistently with the solute electronic density as part of the self-consistent field solution. This covers the bulk electrostatic part of the calculations.

For the non-electrostatic part, most modern models assume a proportionality between the sum of all the remaining effects and the exposed surface area of the solute, with the constant of proportionality being dictated by the nature of the underlying atom or group (and generally determined empirically). More physically based models are available (e.g., scaled-particle theory for cavitation) but less widely used.

Q2) Consider a QM/MM calculation in which the boundary between the two regions does *not* cross any covalent bonds. Describe how computationally the QM and MM regions may be separately or jointly polarized (or not) by the other region. Full mutual polarization is most physically realistic, but why might one choose not to adopt such an approach? What "tricks" might be used to increase the accuracy of a calculation in which one or both regions are unpolarized? (30 points)

Jointly UNpolarized would involve computing the electrostatic interaction between the gas-phase charge distribution of the QM region and the MM region (either by fitting point charges or multipoles to the QM distribution and interacting those with MM partial charges, or by solving electronic integrals interacting with the MM partial charges using gas-phase density matrix elements).

Polarization of the QM region occurs when the MM charge distribution is included as a potential operator in the Hamiltonian (i.e., MM atomic charges look like partially charged nuclei). Polarization of the MM region occurs when polarizability tensors are added to the MM atoms so that the MM atoms can have induced dipole moments that then interact with each other and the remaining charge distribution. When both of these effects are included (which will involve adding dipole operators to the QM Hamiltonian, which is not particularly difficult), full mutual polarization will be included, although it will need to be iterated to self-consistency in any QM SCF step.

That iterative process is expensive – potentially *very* expensive, which is why one might choose to avoid it. One simple trick might be to not include polarization in the QM calculation, but to scale all QM partial atomic charges by a constant factor, e.g., 1.2, to reflect polarization. Another option would be to compute the charge distribution of the QM region with a continuum model turned on (so it polarizes) and then import it into the QM/MM system without further coupling. Many MM force fields used fixed partial charges that have already been optimized for bulk properties, so those force fields have already included polarization through parameterization to experiment.

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Q3) Use one or more potential energy diagrams to illustrate the following concepts in electronic spectroscopy: (i) vertical excitation energy, (ii) fluorescence, (iii) phosphorescence, (iv) Stokes shift, (v) solvatochromism. Within the context of the configuration interaction with single excitations (CIS) theory, how is an electronic excited state represented? (40 points)

Diagrams in various slides in videos VII.iv to VII.vii illustrate concepts i–v and are not reproduced here.

In CIS theory, an excited electronic state is represented as a linear combination of determinants formed from removing one electron from one of the HF occupied orbitals and placing it into one of the HF virtual orbitals. Thus, they are represented in the fashion of the second term on the right-hand side of the more general CI expression below

$$\Psi = a_0 \Psi_{\text{HF}} + \sum_i^{\text{occ.}} \sum_r^{\text{vir.}} a_i^r \Psi_i^r + \sum_{i<j}^{\text{occ.}} \sum_{r<s}^{\text{vir.}} a_{ij}^{rs} \Psi_{ij}^{rs} + \cdots$$

where the coefficients of the linear combination are a and the occupied and virtual orbitals whose occupation is being swapped are indexed by i and r, respectively.

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