

6.7: Molecules Embedded in Condensed Media

Often one wants to model the behavior of a molecule or ion that is not isolated as it might be in a gas-phase experiment. When one attempts to describe a system that is embedded, for example, in a crystal lattice, in a liquid or a glass, one has to have some way to treat both the effects of the surrounding medium on the molecule of interest and the motions of the medium's constituents. In so-called quantum mechanics- molecular mechanics (QM-MM) approaches to this problem, one treats the molecule or ion of interest using the electronic structure methods outlined earlier in this Chapter, but with one modification. The one-electron component of the Hamiltonian, which contains the electron-nuclei Coulomb potential $\sum_{a,i} (-Z_a e^2 / |r_i - R_a|)$, is modified to also contain a term that describes the potential energy of interaction of the electrons and nuclei with the surrounding medium. In the simplest such models, this solvation potential depends only on the dielectric constant of the surroundings. In more sophisticated models, the surroundings are represented by a collection of (fractional) point charges that may also be attributed with local dipole moments and polarizabilities that allow them to respond to changes in the internal charge distribution of the molecule or ion. The locations of such partial charges and the magnitudes of their dipoles and polarizabilities are determined to make the resultant solvation potential reproduce known (from experiment or other simulations) solvation characteristics (e.g., solvation energy, radial distribution functions) in a variety of calibration cases. The book *Molecular Modeling*, 2nd ed., A. R. Leach, Prentice Hall, Englewood Cliffs (2001) offers a good source of information about how these terms are added into the one-electron component of the Hamiltonian to account for solvation effects.

In addition to describing how the surroundings affect the Hamiltonian of the molecule or ion of interest, one needs to describe the motions or spatial distributions of the medium's constituent atoms or molecules. This is usually done within a purely classical treatment of these degrees of freedom. That is, if equilibrium properties of the solvated system are to be simulated, then Monte-Carlo (MC) sampling (this subject is treated in Chapter 7 of this text) of the surrounding medium's coordinates is used. Within such a MC sampling, the potential energy of the entire system is calculated as a sum of two parts:

- i. the electronic energy of the solute molecule or ion, which contains the interaction energy of the molecule's electrons and nuclei with the surrounding medium, plus
- ii. the intra-medium potential energy, which is taken to be of a simple molecular mechanics (MM) force field character (i.e., to depend on inter-atomic distances and internal angles in an analytical and easily computed manner). Again, the book *Molecular Modeling*, 2nd ed., A. R. Leach, Prentice Hall, Englewood Cliffs (2001) offers a good source of information about these matters.

If, alternatively, dynamical characteristics of the solvated species are to be simulated, a classical molecular dynamics (MD) treatment is used. In this approach, the solute-medium and internal-medium potential energies are handled in the same way as in the MC case but where the time evolution of the medium's coordinates are computed using the MD techniques discussed in Chapter 7 of this text.

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