Quantum chemical modelling of molecular properties - modelling of solvent effects
The concept of solvent effects

Spectroscopic measurements are usually carried in liquid phase, and observables are affected by this fact. The concept of ‘solvent effects’ relies on the assumption that properties of a solute and its environment can be treated separately. (Which is not always the case: for extensive properties, such as electric dipole polarizability or optical rotation, separation of a solute and solvent is difficult.)

Solvent effects are usually defined as a difference between the value of a given molecular property in solution and in diluted gas (or another medium assumed ‘non-interacting’).
Direct and indirect solvent effects

Solvent effects can be divided (somewhat artificially, in calculations only, assuming Born-Oppenheimer approximation) into direct (caused by modification of electronic density of the solute and fields acting on the solute by the presence of a solvent) and indirect (caused by modification of electronic density by a solvent) effects.

The relative weights of direct and indirect effects differ depending on the solute, solvent and property, but generally both should be accounted for in the calculations.
Approaches for modelling of solvent effects

Solvent can be modelled by means of

- Explicit models (solvent molecules treated at the same footing as the solute). Solute-solvent clusters can be generated by means of:
  - geometry optimization,
  - molecular dynamics,
  - other methods (utilizing e.g. information from experiment).

- Implicit models:
  - polarizable continuum model (PCM) and its variations, where the solvent is treated as a continuous medium (dielectric or conductor-like),
  - neighbouring solvent molecules modelled as a discreet assembly of charges or point dipoles (position of the charges or point dipoles are obtained in similar manner as for explicit models).
Models are often combined (e.g., the first solvation shell is treated by means of quantum chemical methods, like the solute, the second is modeled as assembly of charges, the rest as a continuum). ONIOM method (molecular orbital + molecular mechanics) available in Gaussian is one of such combined models.

The same approaches as for solvent effects can be used for modeling of the influence of a protein (or nucleic acids/zeolite/etc) environment on the moiety of interest.
Advantages and disadvantages of explicit and implicit models

Explicit models are conceptually easy, can be applied in principle for any system (including hydrogen bonded systems), do not require any additional programming (basically the calculations are performed for a solute-solvent supermolecular cluster), but they are very resource-consuming. It is not possible to take into account long-range or bulk solvent effects in this manner. Usually, it is necessary to carry our calculations for a large number of solute-solvent clusters (further expenditure of computational resources) and average out the results.

Implicit models are computationally cheap and allow to take into account long-range or bulk solvent effects. On the other hand, they do not allow for accurate treatment of specific solvent effects, and they are sometimes difficult to implement. One needs to pay attention to a proper description of the physics of the system (avoid artifacts in continuum models, pay attention to balance out Coulombic forces with valence repulsion for discrete models).
Usually the best way is to combine the two approaches.
Continuum models

There are several continuum models in use. They can be described by:

- the construction of cavity,
- the potential describing the interaction with the bulk environment added to the Hamiltonian.
Cavity

The cavity can be constructed as:

- Sphere or ellipsoid, with the size depending on the size of the molecule (eg. so-called reaction field model by Mikkelsen et al.). Rarely used nowadays because of a narrow range of applications.

- Assembly of interlocking spheres centered on atoms (all atoms or excluding hydrogens). The most popular models (IEF-PCM and C-PCM in Gaussian, COSMO) are constructed in this way.

- A smooth surface following the shape of the molecule, eg. electron isodensity surface (eg. SCI-PCM).

Exact size of the cavity (eg. sphere radii) is always a problem and usually is arbitrary.
Interaction Hamiltonian

Considering the potential, the continuum models can be divided in the following manner:

- Polarized continuum model (PCM) with apparent surface charges (ASC), developed primarily in the groups of Tomasi. In this approach, the cavity is made from spheres centered on nuclei in the solute molecule, and the cavity surface is divided into a number of small surface elements, where the reaction field is modeled by distributing charges onto the surface elements, by creating apparent surface charges. The electrostatic part of the solvent-solute interaction represented by the charge density spread over the cavity surface gives rise to an operator to be added to the Hamiltonian of the isolated system. Both IEF-PCM (Integral Equation Formalism) and SCI-PCM (Self-Consistent Isodensity) work in this way.

- COSMO method (*Conductorlike Screening MOdel*) by Klamt and coworkers in which the surrounding medium is modeled as
a conductor instead of a dielectric (that is, it uses scaled conductor boundary condition instead of the dielectric boundary condition for the calculation of the polarization charges of a molecule in a continuum). A variation on the COSMO model is C-PCM (available in Gaussian).

- MPE (multipole expansion method) by Rivail and Rinaldi and related reaction field method by Mikkelsen and co-workers - the polarization of a solute by dielectric environment (and vice versa) is described by multipole expansion (thus analytically). This method an be used only with a cavity of regular shape (spherical, elipsoid).