Computational Material Science
Part I

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Review of Hartree-Fock MO Theory

- Wavefunction: Slater determinant

  For the general case (use χ to express both the spatial and spin parts of the equation)

$$\Psi_{\mathrm{SD}} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(N) & \chi_2(N) & \cdots & \chi_N(N) \end{vmatrix}$$

- Operator

$$f_i = \underline{-\frac{1}{2}\nabla_i^2 - \sum_k^{\text{nuclei}} \frac{Z_k}{r_{ik}}} + \underline{V_i^{\mathrm{HF}}\{j\}}$$

Two electron part (will give Coulomb integral, J, and exchange integral, K)

One electron part (will give H_{core})

- Notation of theory level:
  - HF/6-31+G* (optimization)
  - HF/6-31+G*//HF/6-31G* (single point calculation)

- Coulomb and exchange integrals:

Consider two electron integral of like spin: (α and α)

$$\int {}^3\Psi_{\mathrm{SD}} \frac{1}{r_{12}} {}^3\Psi_{\mathrm{SD}} d\mathbf{r}_1 d\omega_1 d\mathbf{r}_2 d\omega_2$$

$$= \frac{1}{2}\Big[\int |\psi_a(1)|^2\,|\alpha(1)|^2 \frac{1}{r_{12}} |\psi_b(2)|^2\,|\alpha(2)|^2\, d\mathbf{r}_1 d\omega_1 d\mathbf{r}_2 d\omega_2$$

$$- 2\int \psi_a(1)\psi_b(1)\,|\alpha(1)|^2 \frac{1}{r_{12}} \psi_b(2)\psi_a(2)\,|\alpha(2)|^2\, d\mathbf{r}_1 d\omega_1 d\mathbf{r}_2 d\omega_2$$

$$+ \int |\psi_a(2)|^2\,|\alpha(2)|^2 \frac{1}{r_{12}} |\psi_b(1)|^2\,|\alpha(1)|^2\, d\mathbf{r}_1 d\omega_1 d\mathbf{r}_2 d\omega_2\Big]$$

$$= \frac{1}{2}\Big[\underline{\int |\psi_a(1)|^2 \frac{1}{r_{12}} |\psi_b(2)|^2\, d\mathbf{r}_1 d\mathbf{r}_2}$$

$$- 2\underline{\int \psi_a(1)\psi_b(1) \frac{1}{r_{12}} \psi_b(2)\psi_a(2)\, d\mathbf{r}_1 d\mathbf{r}_2}$$

$$+ \underline{\int |\psi_a(2)|^2 \frac{1}{r_{12}} |\psi_b(1)|^2\, d\mathbf{r}_1 d\mathbf{r}_2}\Big]$$

$$= \frac{1}{2}\left(J_{ab} - 2\int \psi_a(1)\psi_b(1) \frac{1}{r_{12}} \psi_a(2)\psi_b(2)\, d\mathbf{r}_1 d\mathbf{r}_2 + J_{ab}\right)$$

$$= J_{ab} - \underline{K_{ab}}$$

***J*: Coulomb integral**

***K*: exchange integral**

only exist for like spin!

- Eigenvalue of operator, ε_i (orbital energy)

  class note

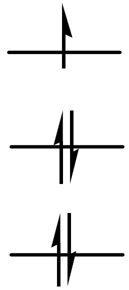
- **E**$_{\textbf{total}}$

  class note

- RHF, ROHF, UHF Wavefunctions
  - **RHF** (spin-restricted), **ROHF** (restricted open-shell HF)

    α and β spins occupy the same spatial orbital

ROHF



ROHF thoery produces wave functions that are eigenfunctions of the spin operator S^2, but fails to account for spin polarization

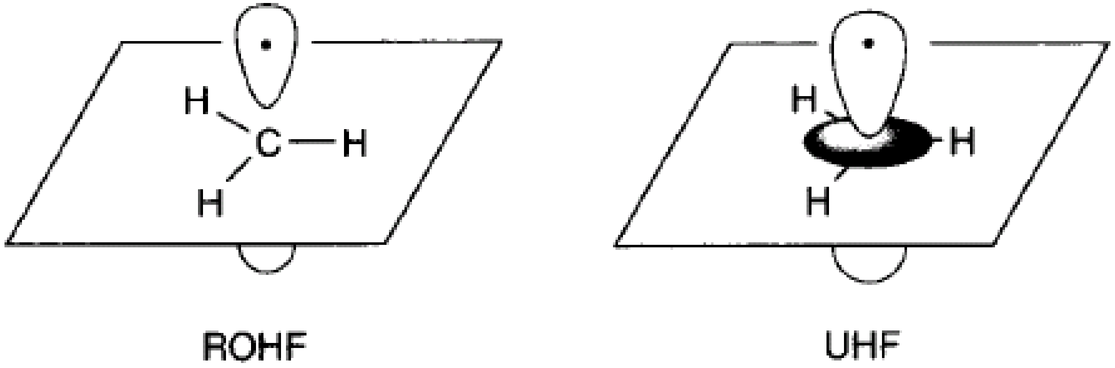
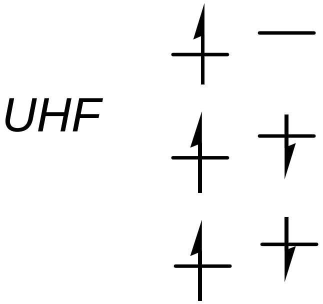


Figure 6.10 In the absence of spin polarization, which corresponds to the ROHF picture, there is zero spin density in the plane containing the atoms of the methyl radical. Accounting for spin polarization, which corresponds to the UHF picture, results in a build-up of negative spin density (represented as a shaded region) in the same plane

- **UHF** (spin-unrestricted)

  α and β spins occupy different spatial orbitals



UHF does *not* produces wave functions that are eigenfunctions of the spin operator S^2, but can account for spin polarization

Spin contamination: UHF wave function incorporates some degree of "contamination" from higher spin states

Doublets contaminated by quartets, sextets, octets…

Triplets contaminated by pentets, heptets, nonets…

Degree of contamination can be judged from <S^2>

Expectation value of the spin operator <S^2> = S(S+1) S = vector sum of spin magnetic moment
0.75 for doublet; 2.00 for triplet; 3.75 for quartet

If <S^2> larger than expected value by 5%, do not use
Problem of spin contamination!

- General strategies for efficient calculations

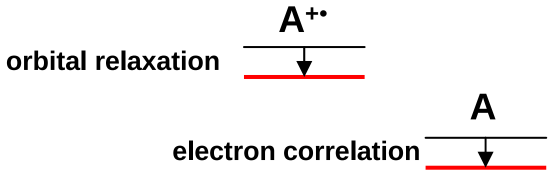
- Use symmetry

Reduce the dimension of degree of freedom and the size of matrix. *Caution: may introduced undesirable constraints*

-**Use wave function, geometry, Hessian matrix (force constants) from lower level results => easier to converge, time saving!**
=> important for large molecules or high level calculations

- Performance of ab initio HF Theory

  - The secret of success of Koopman's theory ($E_{HOMO} = -IP$) (orbital relaxation and the electron correlation effects offset one another)



$$\mathrm{IP}_{\Delta\mathrm{SCF}} = E_{\mathrm{HF}}(\mathrm{A}^{+\bullet}) - E_{\mathrm{HF}}(\mathrm{A})$$

  - Reaction energy: not very good in the absolute values, may be acceptable qualitatively (because electrons are in different bonding situations, less error canceling)

  - Conformer energy difference: ok

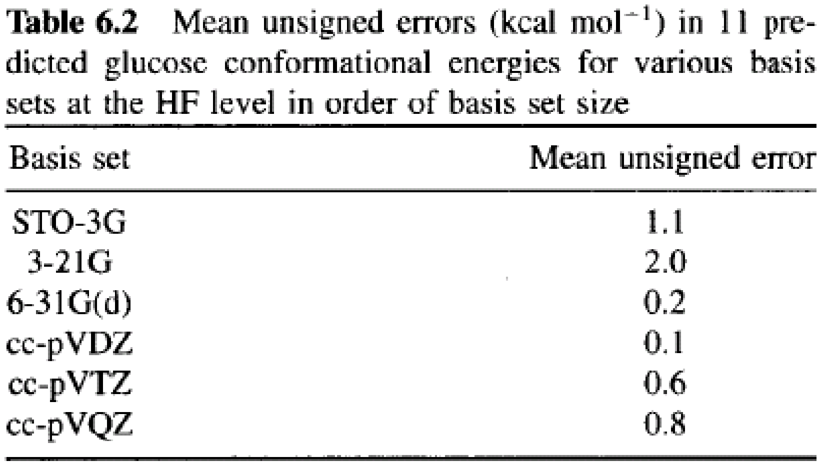


Table 6.2 Mean unsigned errors (kcal mol^{-1}) in 11 predicted glucose conformational energies for various basis sets at the HF level in order of basis set size

Basis set	Mean unsigned error
STO-3G	1.1
3-21G	2.0
6-31G(d)	0.2
cc-pVDZ	0.1
cc-pVTZ	0.6
cc-pVQZ	0.8

Larger basis set may not guarantee better results because basis set incompleteness and failure to account for electron correlation may introduce errors of opposite sign

Best basis set can be determined when closely related systems are studied and compared to experimental results

Charge Distribution Related Issues

- Electric Multipole Moments

Expectation value of multipole momemt operators

$$\langle \mathbf{x}^k \mathbf{y}^l \mathbf{z}^m \rangle = \sum_{i}^{\text{atoms}} Z_i x_i^k y_i^l z_i^m - \int \Psi(\mathbf{r}) \left(\sum_{j}^{\text{electrons}} x_j^k y_j^l z_j^m \right) \Psi(\mathbf{r}) d\mathbf{r}$$

Sum of *k, l*, *m*: 0 = monopole, 1 = dipole, 2 = quadrupole

When k = l = m = 0, the operator is 1

$$\langle \mathbf{1} \rangle = \sum_{i}^{\text{atoms}} Z_i - \sum_{j}^{\text{electrons}} \int \psi_j(\mathbf{r}_j) \psi_j(\mathbf{r}_j) d\mathbf{r}_j$$

$$= \sum_{i}^{\text{atoms}} Z_i - N$$

⇒ Monopole is the difference of sum of nuclear charges and the number of electrons

For a neutral molecule: monopole = 0
cation molecule: monopole = +1
anion molecule: monopole = -1

When k = 1 or l = 1 or m = 1, one gets μ_x, μ_y, and μ_z

Experimentally, <μ> is measured

$$\langle \mu \rangle = \sqrt{\langle \mu_x \rangle^2 + \langle \mu_y \rangle^2 + \langle \mu_z \rangle^2}$$

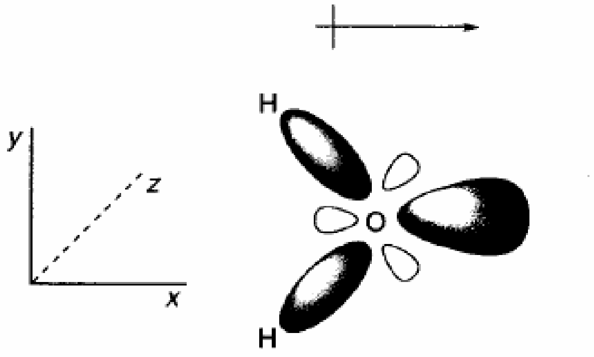


Figure 9.1 Contributions to the dipole moment of the water molecule

⇒ Dipole moment measures the degree to which positive and negative charges are differentially distributed relative to one another

Some neutral symmetrical molecules has zero dipole moment, but has quadruple moment

Ex: CO_2 O=C=O

\- + -

Note: only the first non-zero electric moment of a molecule is independent of origin!

Only the first non-zero electric moment of a molecule is independent of origin!

For a neutral molecule, monopole = 0

q = -1 +1

-r 0 +r

μ **= (-1)(-r) + (+1)(r) = 2r**

q = -1 +1

0 +2r

μ **= (-1)(0) + (+1)(2r) = 2r**

For a cationic molecule, monopole = +1

q = -1 +2

-r 0 +r

μ **= (-1)(-r) + (+2)(r) = 3r**

q = -1 +2

0 +2r

μ **= (-1)(0) + (+2)(2r) = 4r**

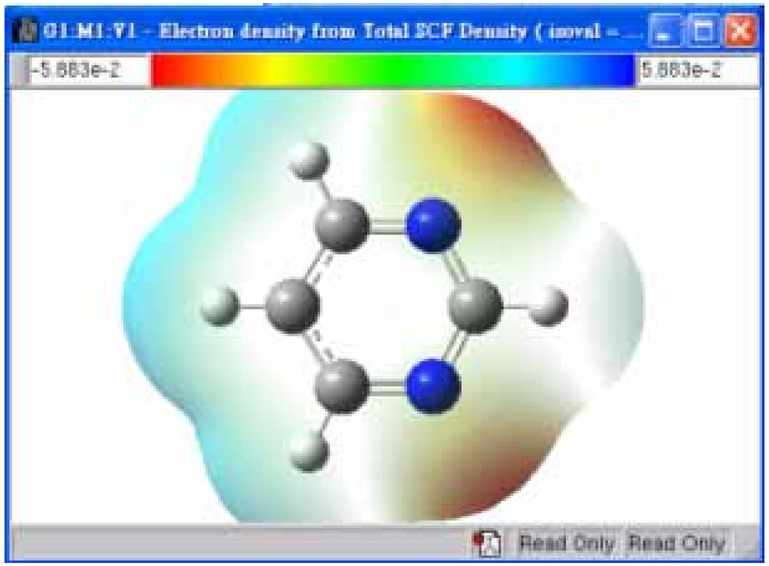
In the cationic case, the origin of dipole should also be reported…
(origin is normally the center of charge or the center of mass)

➢ Molecular Electrostatic Potential (MEP)

$$V_{\mathrm{MEP}}(\mathbf{r}) = \underbrace{\sum_{k}^{\text{nuclei}} \frac{Z_k}{|\mathbf{r}-\mathbf{r}_k|}}_{\text{nuclei}} \underbrace{- \int \Psi(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} \Psi(\mathbf{r}') d\mathbf{r}'}_{\text{electrons}}$$

MEP quantifies the degree to which a positive (+1) test charge is attracted or repelled by the molecule

The value of MEP is often color-coded on van der Waals surface; regions of local polarity can be discerned easily.



Note: no polarization of the molecule in response to the test charge

➢ Partial Atomic Charges

Although not define uniquely, “atomic charge” is a useful concept in rationalizing observed phenomena. (e.g. hydrogen bonds are formed because of interaction between partial positive charge on H and partial negative on O…)

------------------------directly wave function based--------------------------

- **Mulliken population analysis**

Total number of electrons, N

$$
\begin{aligned}
N &= \sum_{j}^{\text{electrons}} \int \psi_j(\mathbf{r}_j)\psi_j(\mathbf{r}_j)d\mathbf{r}_j \\
&= \sum_{j}^{\text{electrons}} \sum_{r,s} \int c_{jr}\varphi_r(\mathbf{r}_j)c_{js}\varphi_s(\mathbf{r}_j)d\mathbf{r}_j \\
&= \sum_{j}^{\text{electrons}} \left(\sum_{r} \underset{\substack{\uparrow \\ \text{from same} \\ \text{atom}}}{c_{jr}^2} + \sum_{r \neq s} c_{jr}c_{js}\underset{\substack{\uparrow \\ \text{from same or} \\ \text{different atoms}}}{S_{rs}} \right)
\end{aligned}
$$

r and *s* index AO basis function; c_{jr} is the coefficient of basis function *r* in MO *j*; S is overlap matrix element

Mulliken suggested that shared electrons between atoms are divided evenly between two atoms

$$N_k = \sum_{j}^{\text{electrons}} \left(\underbrace{\sum_{r\in k} c_{jr}^2 + \sum_{\underline{r,s\in k},r\neq s} c_{jr}c_{js}\overset{\text{0 for orthogonal atomic orbitals}}{\cancel{S_{rs}}}}_{\text{same atom } k} + \underbrace{\sum_{\underline{r\in k,s\notin k}} c_{jr}c_{js}S_{rs}}_{\text{shared between atom } k \text{ and other atoms}} \right)$$

Mulliken partial atomic charge

$$q_k = Z_k - N_k$$

Mulliken charge:

- Useful to show the changes in charge as a function of geometry change or substitution change.
- Basis set dependent. Do not compare values from different basis sets.
- Potentially problematic as electronegativity difference between atoms are not considered
- In reality non-orthogonal atomic orbitals are used; sometimes unphysical charges obtained

- **Löwdin population analysis and Natural population analysis (NPA)**

In these two population analyses, partial atomic charges are not evaluated until AO basis functions being transformed into an orthonormal set of basis functions.

- Less basis set dependent

------------------------*in*directly wave function based--------------------------

- **Generalized atomic polar tensor (GAPT) charge** (based on dipole)

$$q_k = \frac{1}{3}\left(\frac{\partial \mu_x}{\partial x_k} + \frac{\partial \mu_y}{\partial y_k} + \frac{\partial \mu_z}{\partial z_k}\right)$$

  - A theory level fails to give good dipole moments (e.g., HF) is unlikely to give useful charge

- **Atoms-in-molecules charge** (based on density)

Electron density is integrated within an “atomic volume” defined by “zero-flux surfaces” in the gradient vectors of the charge density surrounding the nucleus.

$$q_k = Z_k - \int_{\Omega_k} \rho(\mathbf{r}) d\mathbf{r}$$

How does electron density vary on a molecular plane?

Ex: $H_2C{=}CH_2$

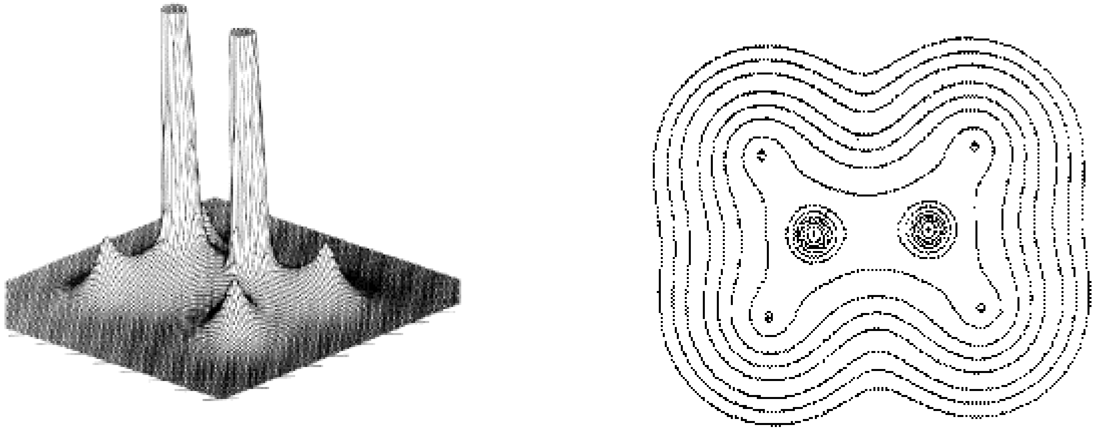


Figure 1. (a) The electron density in the plane containing the two carbon and four hydrogen nuclei of the ethene molecule, portrayed as a projection in the third dimension and in the form of a contour map. The absolute maxima in $\rho(r)$ attained at the positions of the carbon nuclei are not shown because of their large values.

What is gradient vector of density?

A vector that points in the direction of maximum increase in the density.

What are “zero-flux surfaces” ?

“**zero-flux surfaces**” defined as the union of all points for which

$$\nabla\rho \cdot \mathbf{n} = 0$$; **n** is the unit vector normal to the surface

zero-flux surfaces

At this point density gradient is zero

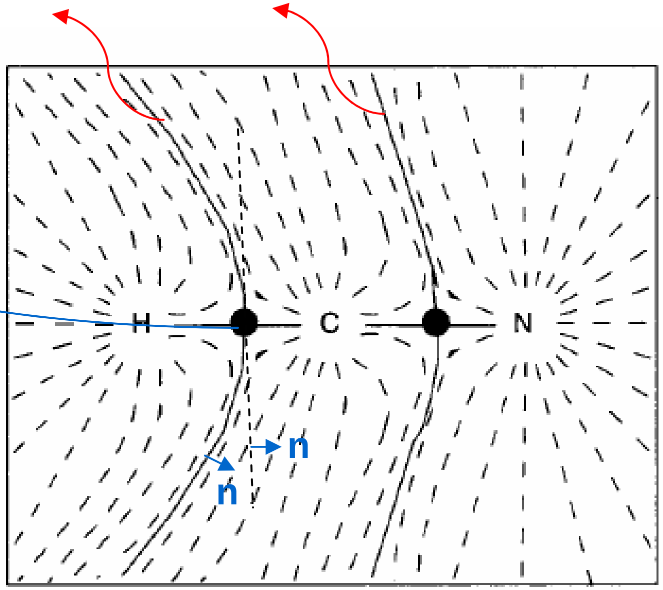


Figure 9.4 Electron density gradient paths in a plane containing the atoms of the HCN molecule. The solid lines are the intersections of the zero-flux surfaces with the plane. The large black dots are the bond critical points

- **ESP (electrostatic potential) charge** (based on MEP)

Determine atomic partial charges (q_k) that minimize the difference between $\boldsymbol{V}_{\mathbf{ESP}}$ and the correct $\boldsymbol{V}_{\mathbf{MEP}}$.

$$V_{\mathrm{ESP}}(\mathbf{r}) = \sum_{k}^{\text{nuclei}} \frac{q_k}{|\mathbf{r} - \mathbf{r}_k|}$$

- Select a large number of points spaced evenly on a cubic grid surrounding the van der Waals surface of the molecule.
- The two most widely used algorithms are by Breneman and Wiberg (CHELPG) and by Besler, Merz, and Kollman.
- Provide useful charges to be used in modeling molecule-molecule interactions at short to long range.

- **CM*x* charge** (fitting experimental dipole)

Modify Mulliken charge to reproduce experimental dipole

CM1: based on AM1 or PM3 charges
CM2 and CM3: based on AM1, PM3, HF, and DFT charges

Implicit Models for Condensed Phases

- Condensed-phase Effects

Ex: Changes in dipole moments

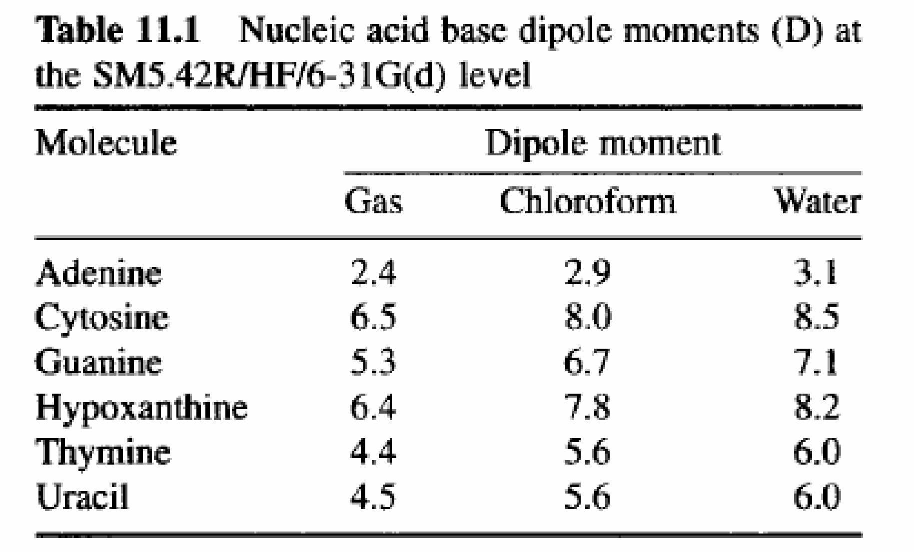


Table 11.1 Nucleic acid base dipole moments (D) at the SM5.42R/HF/6-31G(d) level

Molecule	Dipole moment		
	Gas	Chloroform	Water
Adenine	2.4	2.9	3.1
Cytosine	6.5	8.0	8.5
Guanine	5.3	6.7	7.1
Hypoxanthine	6.4	7.8	8.2
Thymine	4.4	5.6	6.0
Uracil	4.5	5.6	6.0

Could have significant change in solution (up to 35% change relative to gas phase)

Ex: Change in potential energy surfaces

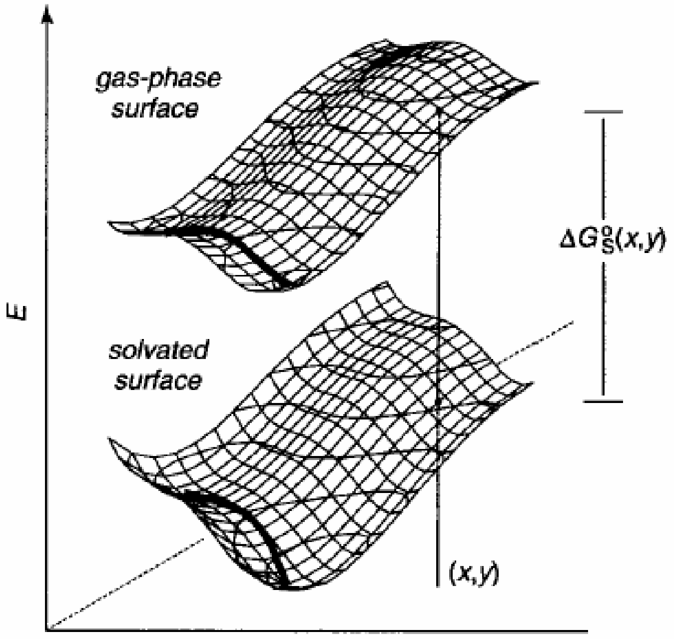


Figure 11.1 A two-dimensional gas-phase PES and the corresponding PES derived from adding the free energy of solvation to every point. This process is illustrated for point (x,y). Thick lines on the two surfaces indicate some chemical reaction proceeding from one minimum-energy structure to another. Note that there is no requirement for the x and y coordinates of equivalent stationary points on the two surfaces to be the same

Note the relative positions of reactant, transition state and product are different (see the thick lines)

=> Reaction energy and rate are different in gas phase and in solution

Ex: Change in potential energy surfaces

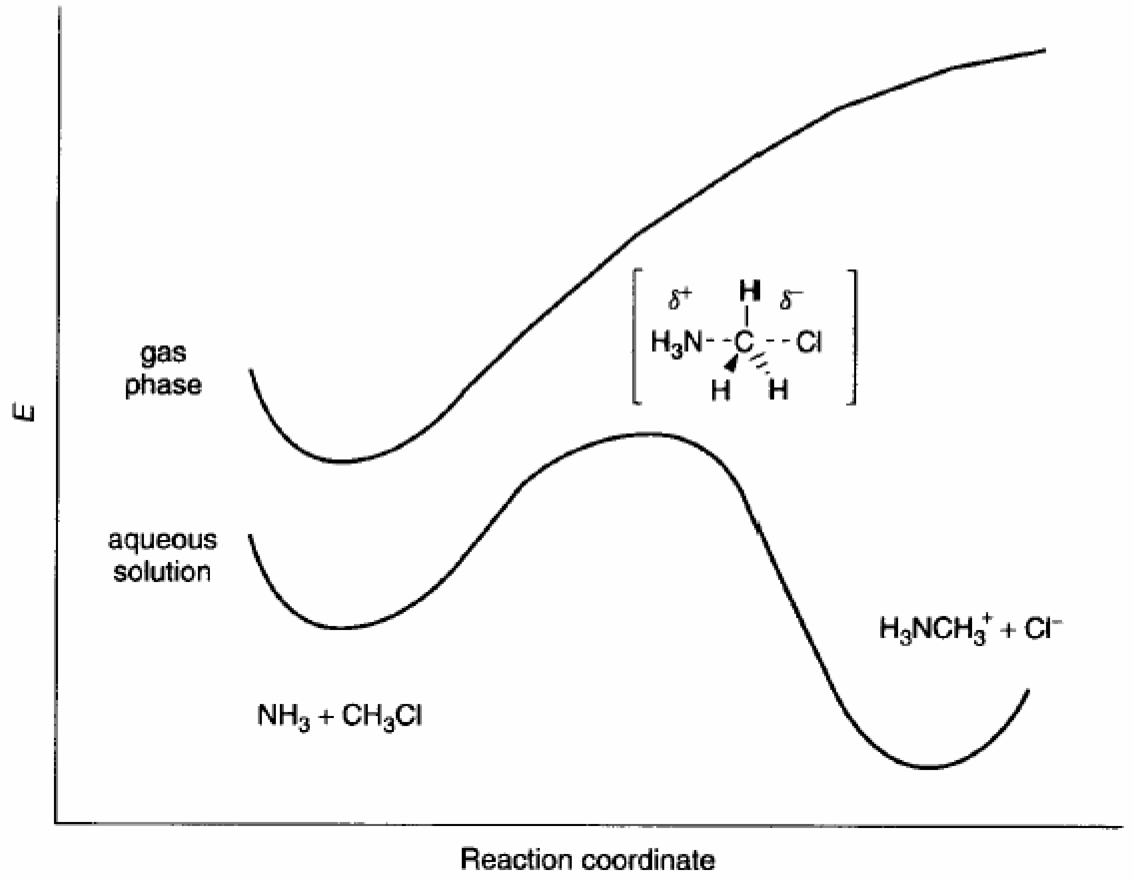
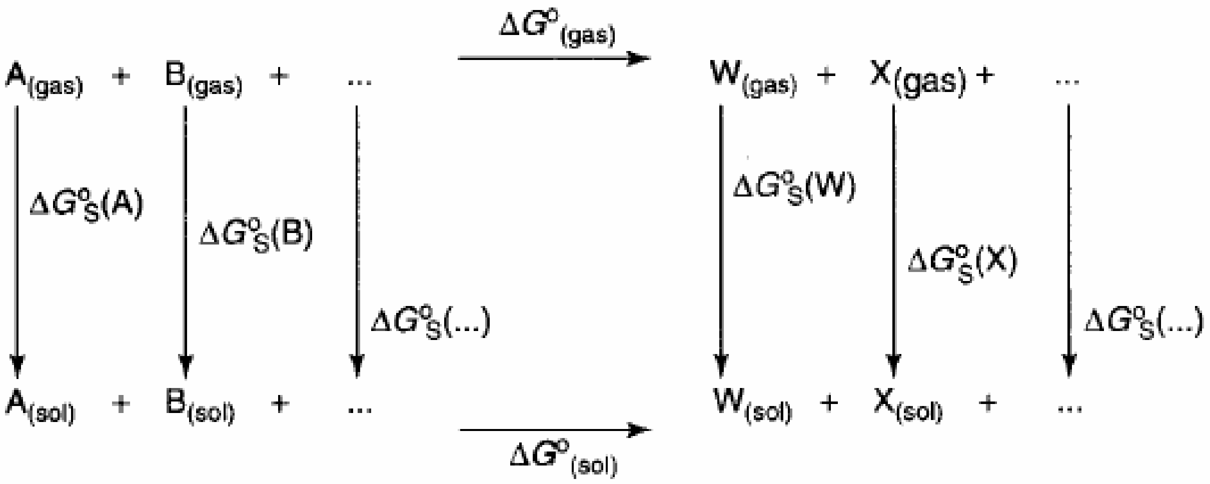


Figure 11.6 Menschutkin reaction of ammonia and chloromethane. In the gas phase nucleophilic displacement fails to take place, while in water solvation of the anions allows the reaction to proceed

How to obtain $\Delta G^o_{(sol)}$ (reaction free energy) ?



$$\begin{tikzcd}
A_{(gas)} \arrow[d, "\Delta G^o_S(A)"] & + & B_{(gas)} \arrow[d, "\Delta G^o_S(B)"] & + & \cdots \arrow[d, "\Delta G^o_S(\ldots)"] \arrow[r, "\Delta G^o_{(gas)}"] & W_{(gas)} \arrow[d, "\Delta G^o_S(W)"] & + & X(gas) \arrow[d, "\Delta G^o_S(X)"] & + & \cdots \arrow[d, "\Delta G^o_S(\ldots)"] \\
A_{(sol)} & + & B_{(sol)} & + & \cdots \arrow[r, "\Delta G^o_{(sol)}"'] & W_{(sol)} & + & X_{(sol)} & + & \cdots
\end{tikzcd}$$

Figure 11.3 Cycle for computation of a free-energy change in solution

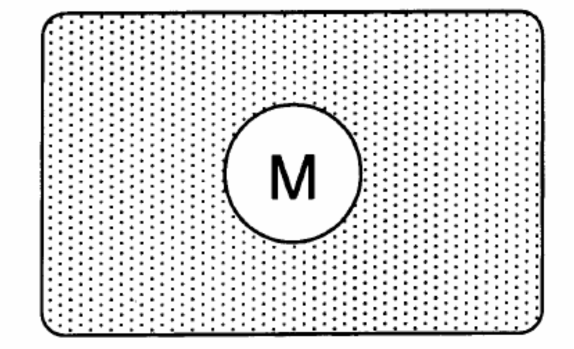
$$\Delta G^o_{(sol)} = \Delta G^o_{(gas)} + \left[\Delta G^o_S(W) + \Delta G^o_S(X) + \cdots\right] - \left[\Delta G^o_S(A) + \Delta G^o_S(B) + \cdots\right]$$

In addition to $\Delta G^o_{(gas)}$ that you get from quantum mechanical calculations, you need to know the free energy difference between gas and solution phases for all solutes ($\Delta G_{solvation}$)…

Solvation free energy $\Delta G_{solvation}$

$$\Delta G_{sol} = \boxed{\Delta G_{cav} + \Delta G_{vdW}} + \Delta G_{elec}$$

$$\boxed{\Delta G_{cav} + \Delta G_{vdW}} = \Sigma\ \sigma_k SA_k$$



SA_k : solvent-accessible surface area

σ_k : empirical atomic solvation parameter

ΔG_{elec} can be evaluated with explicit consideration of solvent molecules. However, it is not clear how many solvent molecules should be included and it is time-consuming to do ab initio or DFT calculations with explicit solvent molecules.

Can solvent effect be included in Hamiltonian in some ways?

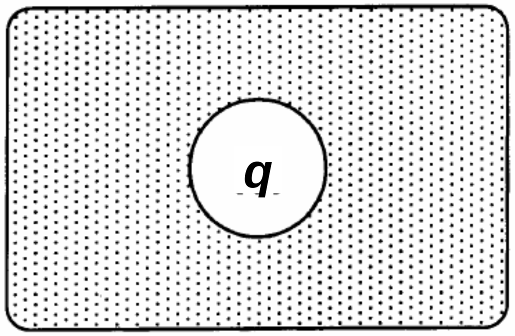
➢ Electrostatic Interactions with a Continuum

Solute and solvent molecules will polarize each other.
Replace explicit solvent molecules by a continuous electric field
that represents a statistical average at thermal equilibrium.
Weakness: Specific interactions (such as hydrogen bond) not considered…

What is free energy? Need electron density and electrostatic potential

$$G = -\frac{1}{2}\int \underbrace{\rho(\mathbf{r})}_{\substack{\downarrow \\ \text{electron} \\ \text{density}}} \underbrace{\phi(\mathbf{r})}_{\substack{\downarrow \\ \text{electrostatic} \\ \text{potential}}} d\mathbf{r}$$

Consider an atomic ion (radius *a*) bearing charge *q*



=> surface charge density ρ(s)

$$\rho(\mathbf{s}) = \frac{q}{4\pi a^2}$$

=> electrostatic potential at the surface ϕ(r)

$$\phi(\mathbf{r}) = -\frac{q}{\underline{\varepsilon}\,|\mathbf{r}|}$$

↓

solvent dielectric constant (solvent effect comes in!)

=> Free energy *G*

$$G = -\frac{1}{2}\int\left(\frac{q}{4\pi a^2}\right)\left(-\frac{q}{\varepsilon a}\right)ds = \frac{q^2}{2\varepsilon a}$$

ε = 1 in gas phase

=> Solvation free energy (G_{solution} – G_{gas}) G_{p}

$$G_{\text{P}} = -\frac{1}{2}\left(1-\frac{1}{\varepsilon}\right)\frac{q^2}{a}$$

Born equation

When Dipole μ occupies the same sphere (*Kirkwood-Onsager equation*)

$$G_P = -\frac{1}{2}\left[\frac{2(\varepsilon-1)}{(2\varepsilon+1)}\right]\frac{\mu^2}{a^3}$$

In the quantum mechanical calculations, wave function and the dipole moment operator determine the dipole moment.

Put Kirkwood-Onsager energy operator in Hamiltonian:

$$\left\{H - \frac{1}{2}\left[\frac{2(\varepsilon-1)}{(2\varepsilon+1)}\right]\frac{\langle\Psi|\underline{\mu}|\Psi\rangle}{a^3}\underset{\downarrow}{\underline{\mu}}\right\}\Psi = E\Psi$$

Dipole moment operator

The final wave function must render stationary density matrix and dipole moment.

-- **Self-consistent reaction field (SCRF) calculation**

Solvation free energy -- difference between gas and solution phases:

$$\Delta G_{\mathrm{ENP}} = \underbrace{\left[\langle\Psi^{(\mathrm{sol})}|H|\Psi^{(\mathrm{sol})}\rangle + \langle\Psi^{(\mathrm{sol})}|G_{\mathrm{P}}|\Psi^{(\mathrm{sol})}\rangle\right]}_{\text{solution}} - \underbrace{\langle\Psi^{(\mathrm{gas})}|H|\Psi^{(\mathrm{gas})}\rangle}_{\text{gas}}$$

Involve nucleus (N) and electron (E) dislocation

$$= \Delta E_{\mathrm{EN}} + G_{\mathrm{P}}$$

Note: in some SCRF calculations, geometry is not reoptimized, so nucleus does not relocate.

Two factors contribute to solvation free energy due to electrostatic interaction between solvent and solute: polarization energy G_p and distorsion energy ΔE_{EN}

Generalize Kirkwood-Onsager equation to include higher multipole moments:

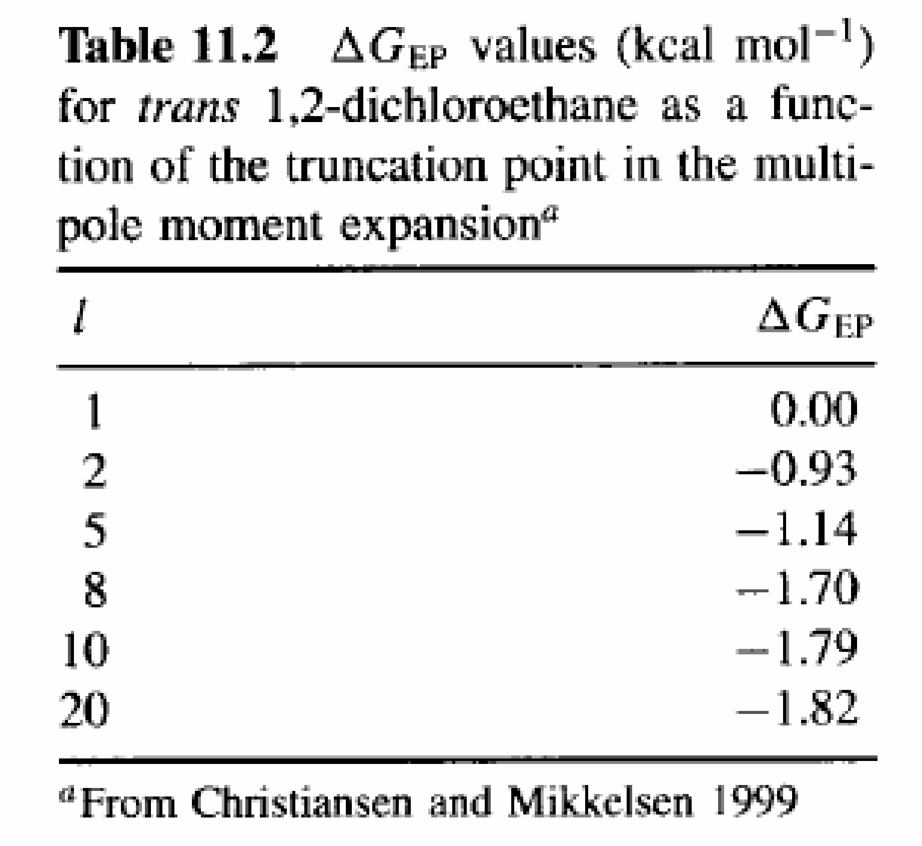


Table 11.2 ΔG_{EP} values (kcal mol^{-1}) for *trans* 1,2-dichloroethane as a function of the truncation point in the multipole moment expansion[a]

l	ΔG_{EP}
1	0.00
2	−0.93
5	−1.14
8	−1.70
10	−1.79
20	−1.82

[a] From Christiansen and Mikkelsen 1999

Problems:

Higher multipole moments are needed!

Not clear about how to determine *a* (cavity size).

In practice: the Polarizable Continuum Model (PCM) by Tomasi

- **Replace ideal cavity shape (sphere) with molecular shape**
- **Assign apparent point charges on surfaces**

Solution wave function determined by

$$\mathscr{H}(\Psi)\Psi = E\Psi$$

$$\mathscr{H}(\Psi) = \mathscr{H}^0 + \mathscr{V}(\Psi)$$

Solute-solvent interaction potential

Hamiltonian of isolated gas phase molecule

$\mathscr{V}(\Psi)$: written in terms of apparent point charges placed at the center of small surface elements (tesserae) on the cavity surface

Number of tesserae and "molecular shape" influences the accuracy of the results…

Chemical Physics Letters 255 (1996) 327–335

One way to generate surface element :

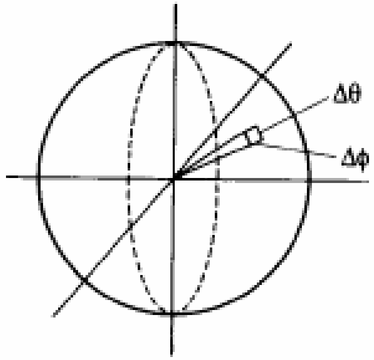


Fig. 9.15 Small surface elements can be created on the van der Waals surface of an atom using constant increments of the polar angles, θ and ϕ.

Apparent point charge on surface $\underline{\sigma(\mathbf{r}_s)}$

$$4\pi\varepsilon\underline{\sigma(\mathbf{r}_s)} = (\varepsilon - 1)\mathbf{F}(\mathbf{r}_s)$$

$\sigma(\mathbf{r}_s)$ *obtained by dielectric constant and electric field perpendicular to the surface,* $\mathbf{F}(\mathbf{r}_s)$, *generated by the charge distribution within the cavity*

$$\mathscr{V}(\Psi) = \int \frac{\sigma(\mathbf{r}_s)}{|\mathbf{r} - \mathbf{r}_s|} d\mathbf{r}_s$$

Ex: Molecular shape determined by van der Waals radii

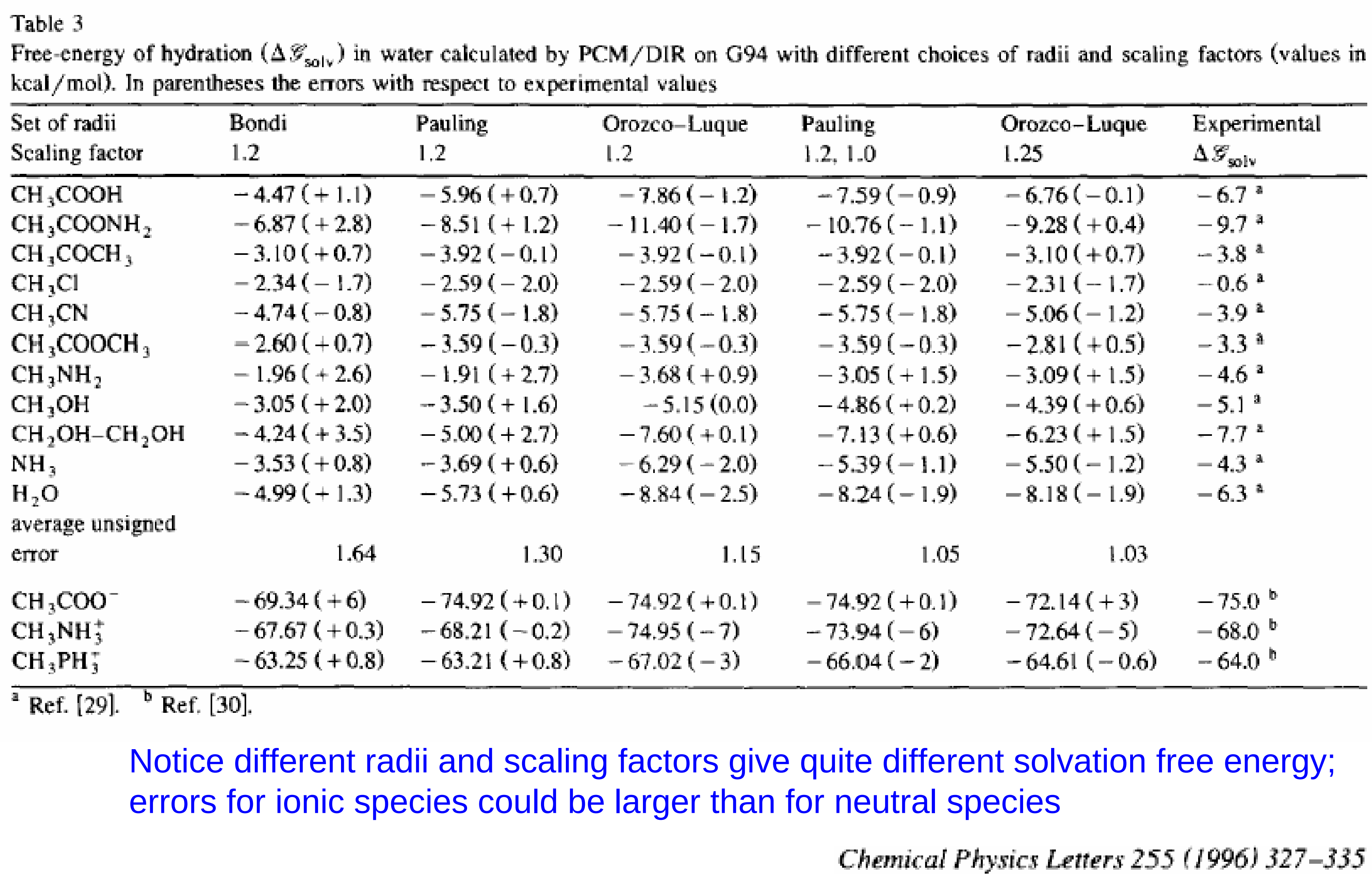


Table 3

Free-energy of hydration ($\Delta \mathscr{G}_{solv}$) in water calculated by PCM/DIR on G94 with different choices of radii and scaling factors (values in kcal/mol). In parentheses the errors with respect to experimental values

Set of radii Scaling factor	Bondi 1.2	Pauling 1.2	Orozco–Luque 1.2	Pauling 1.2, 1.0	Orozco–Luque 1.25	Experimental $\Delta \mathscr{G}_{solv}$
CH_3COOH	−4.47 (+1.1)	−5.96 (+0.7)	−7.86 (−1.2)	−7.59 (−0.9)	−6.76 (−0.1)	−6.7 [a]
CH_3COONH_2	−6.87 (+2.8)	−8.51 (+1.2)	−11.40 (−1.7)	−10.76 (−1.1)	−9.28 (+0.4)	−9.7 [a]
CH_3COCH_3	−3.10 (+0.7)	−3.92 (−0.1)	−3.92 (−0.1)	−3.92 (−0.1)	−3.10 (+0.7)	−3.8 [a]
CH_3Cl	−2.34 (−1.7)	−2.59 (−2.0)	−2.59 (−2.0)	−2.59 (−2.0)	−2.31 (−1.7)	−0.6 [a]
CH_3CN	−4.74 (−0.8)	−5.75 (−1.8)	−5.75 (−1.8)	−5.75 (−1.8)	−5.06 (−1.2)	−3.9 [a]
CH_3COOCH_3	−2.60 (+0.7)	−3.59 (−0.3)	−3.59 (−0.3)	−3.59 (−0.3)	−2.81 (+0.5)	−3.3 [a]
CH_3NH_2	−1.96 (+2.6)	−1.91 (+2.7)	−3.68 (+0.9)	−3.05 (+1.5)	−3.09 (+1.5)	−4.6 [a]
CH_3OH	−3.05 (+2.0)	−3.50 (+1.6)	−5.15 (0.0)	−4.86 (+0.2)	−4.39 (+0.6)	−5.1 [a]
$CH_2OH–CH_2OH$	−4.24 (+3.5)	−5.00 (+2.7)	−7.60 (+0.1)	−7.13 (+0.6)	−6.23 (+1.5)	−7.7 [a]
NH_3	−3.53 (+0.8)	−3.69 (+0.6)	−6.29 (−2.0)	−5.39 (−1.1)	−5.50 (−1.2)	−4.3 [a]
H_2O	−4.99 (+1.3)	−5.73 (+0.6)	−8.84 (−2.5)	−8.24 (−1.9)	−8.18 (−1.9)	−6.3 [a]
average unsigned error	1.64	1.30	1.15	1.05	1.03	
CH_3COO^-	−69.34 (+6)	−74.92 (+0.1)	−74.92 (+0.1)	−74.92 (+0.1)	−72.14 (+3)	−75.0 [b]
$CH_3NH_3^+$	−67.67 (+0.3)	−68.21 (−0.2)	−74.95 (−7)	−73.94 (−6)	−72.64 (−5)	−68.0 [b]
$CH_3PH_3^+$	−63.25 (+0.8)	−63.21 (+0.8)	−67.02 (−3)	−66.04 (−2)	−64.61 (−0.6)	−64.0 [b]

[a] Ref. [29]. [b] Ref. [30].

Notice different radii and scaling factors give quite different solvation free energy; errors for ionic species could be larger than for neutral species

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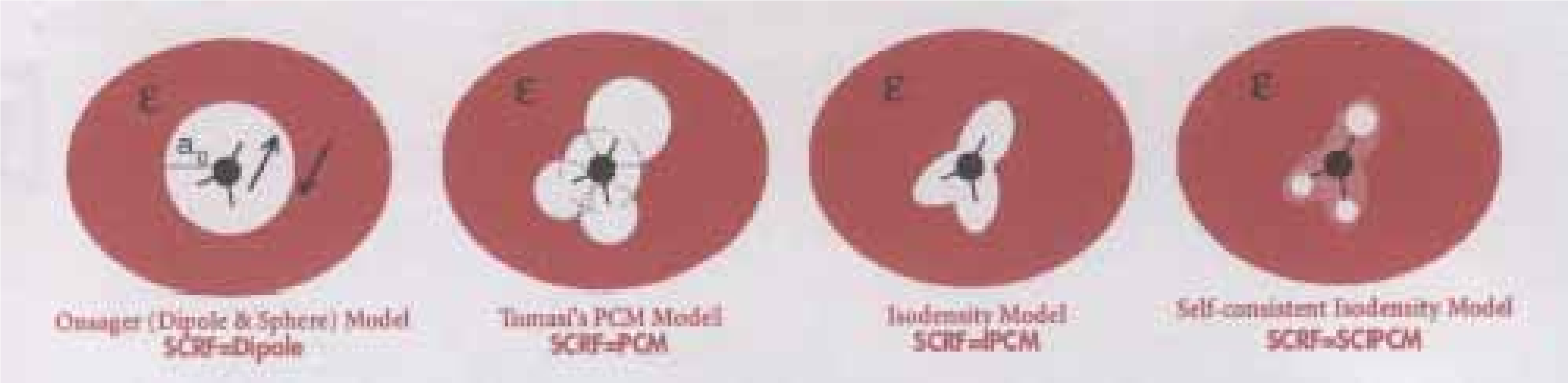
In Gaussian:



Use vdW radii to determine molecular shape

Use isodensity surface from gas phase wave function as molecular shape

Get isodensity surface self-consistently

Other continuum approaches

- **Generalized Born: SMx models by Cramer and Truhlar**

  Mulliken, CM2, CM3 atomic charges used

- **Conductor-like Screening Model: COSMO by Klamt and Schüürmann**

  Assume medium is conducting, image charge develops on the conductor surface in contact with the solute. (This simplifies the necessary electrostatic equations for calculation of polarization free energy and associated energy derivatives.) After evaluation of polarization free energy, scaled by a factor of $2(\varepsilon - 1)/(2\varepsilon + 1)$.

Assignment

- Calculate the following systems

System 1: Choose a molecule (e.g. CH_2F-CH_2-O-H) and two theory levels (e.g. one semiempirical and one HF/3-21G(*)), report how many conformers you have found and report their relative energies at each theory level. Do the two levels predict the same global minimum?

Define dihedral angles, so that you can represent each conformer clearly. For example, ω(F-C-C-O) is ω1 and ω(C-C-O-H) is ω2. **Conf(30,60)** means the ω1 of this optimized conformer is 30° and ω2 is 60°.

System 2: a. Optimize a water molecule at the HF/6-31G* level. Report the energy, structure, Mulliken charges, MEP, HOMO and LUMO of the water molecule. b. Calculate the binding energy of a water dimer at the same theory level, with basis set superposition error corrected. Report the structure of the dimer and compare the geometric parameters with that of the monomer. (You will obtain more points if you locate more than one water dimer structure.)

Note: Frequency analysis has to be carried out for all optimizations to make sure that you have converged to a local minima. Always check whether imaginary frequencies are present.