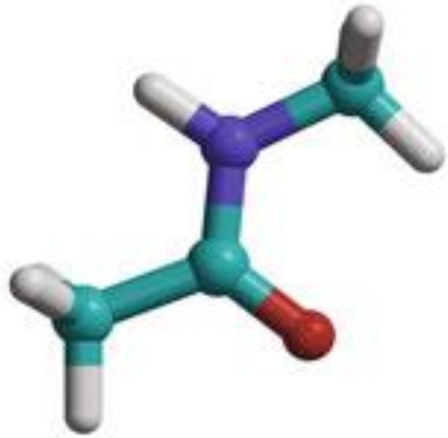
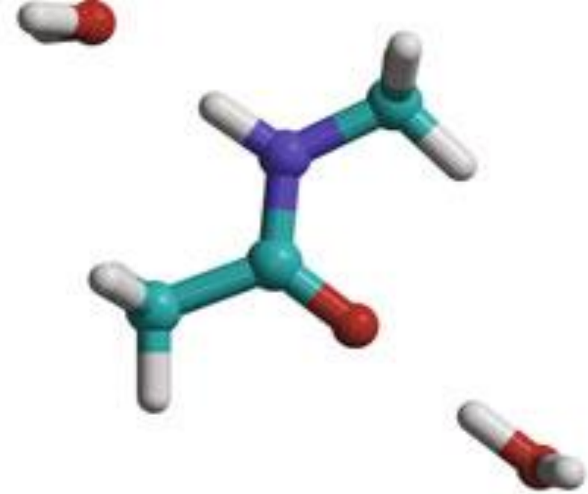
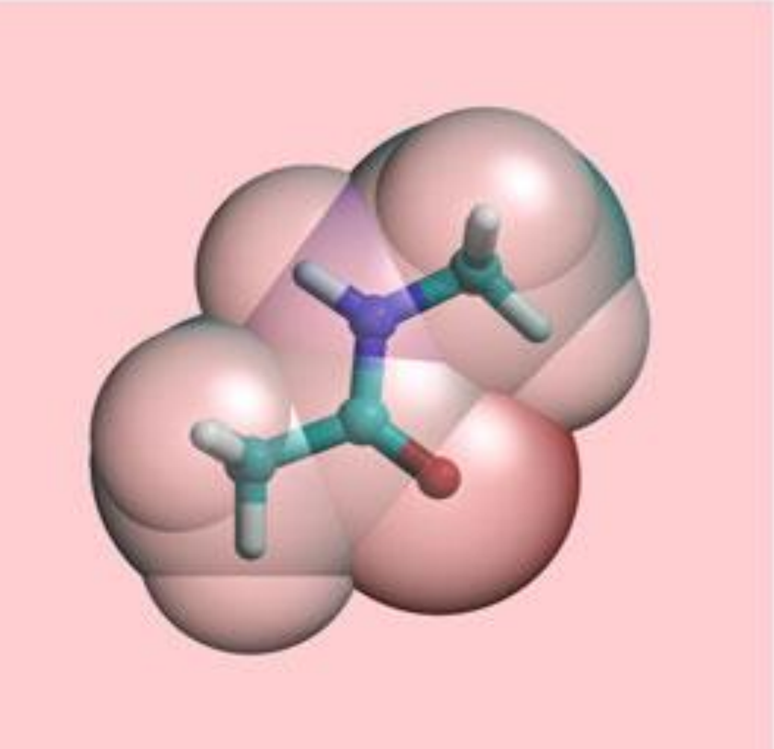
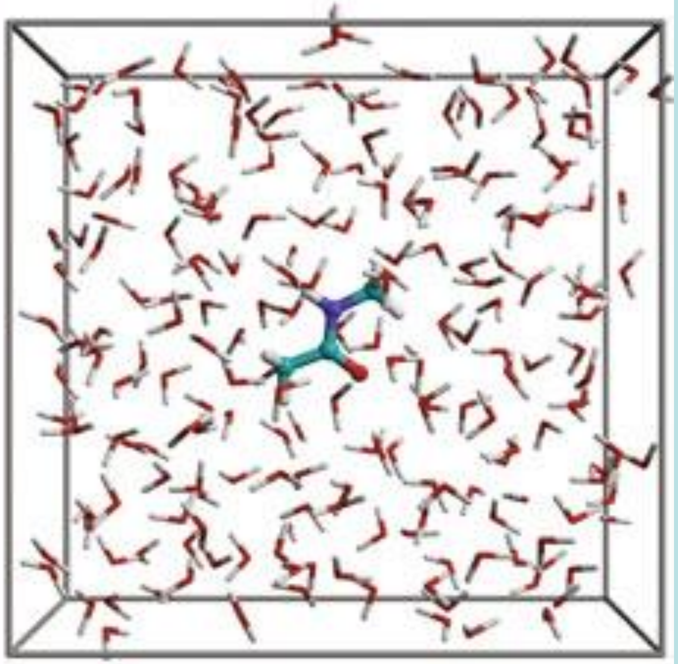
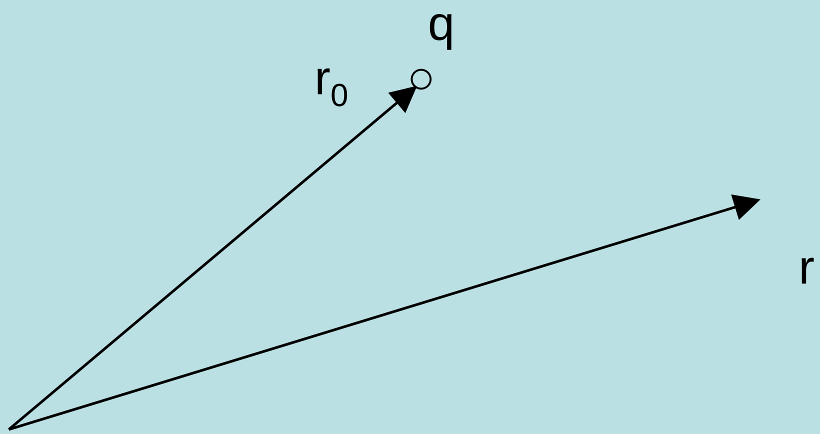
Chemical Materials Department

Environment effects in quantum chemistry (implicit models)

V. V. Ivanov

Chemical Materials Department
V. N. Karazin National University,
61077, Kharkov, Ukraine
vivanov@karazin.ua

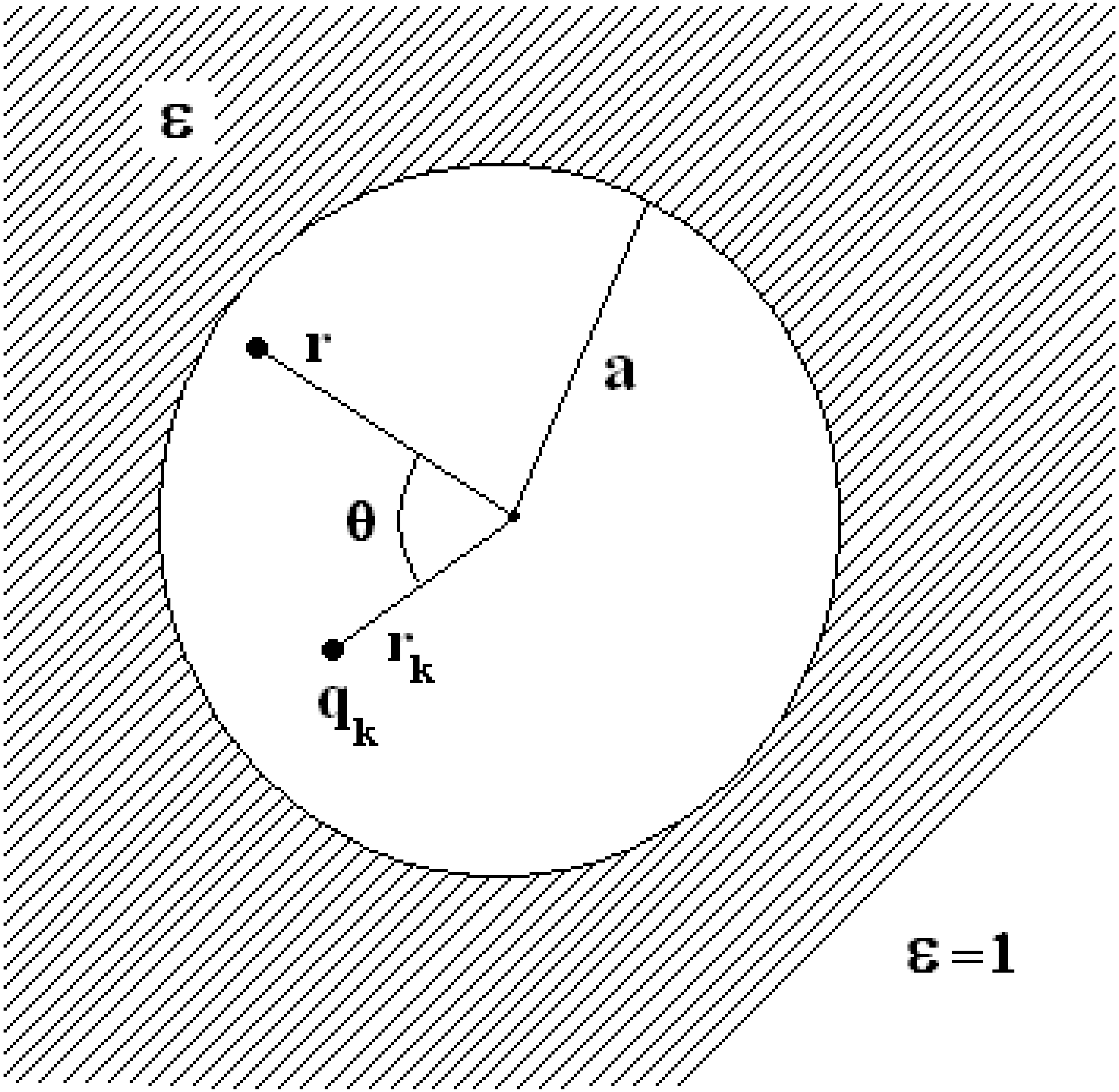


in SI : $$U(r)=\frac{1}{4\pi\varepsilon\varepsilon_0}\frac{q}{|r-r_0|}$$

in СГСЕ: $$U(r)=\frac{1}{\varepsilon}\frac{q}{|r-r_0|}$$

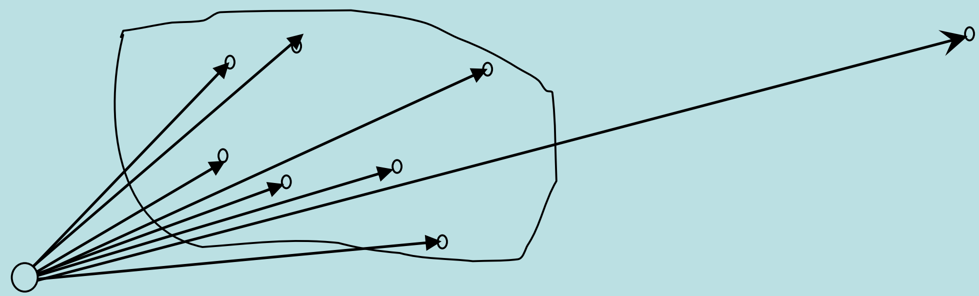
$$\varepsilon_0=8.8541187817\cdot 10^{-12}\Phi/m$$

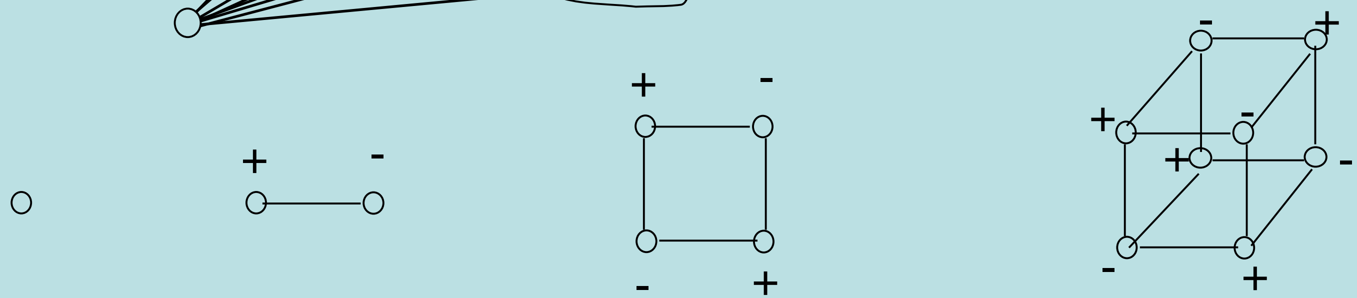
Relative dielectric susceptibility $\varepsilon=1$


ε
r
a
θ
r_k
q_k
ε =1


John G. Kirkwood

Multipole expansion





Charge (monopole) | Dipole | Quadrupole | Octupole

$$q = \sum_i q_i \qquad \mu = \sum_i q_i r_i \qquad Q_{\alpha\beta} = \tfrac{1}{2} \sum_i q_i \left(3x_{i\alpha} x_{i\beta} - \delta_{\alpha\beta} r_i^2\right)$$

$$V(r) = \sum_i \frac{q_i}{|r - r_i|} = \frac{q}{r} + \frac{\mu \cdot r}{|r|^3} + \sum_{\alpha\beta=1,2,3} Q_{\alpha\beta} \frac{x_\alpha x_\beta}{|r|^5} + \ldots$$

J. G. Kirkwood, 1932

$$V(r) = \sum_{k=1}^{M} \frac{q_k}{|r - r_k|} + \underbrace{\sum_{k=1}^{M} \left(\frac{q_k}{a}\right) \sum_{\ell=0}^{\infty} \left[\frac{(\ell+1)(1-\varepsilon)}{\varepsilon(\ell+1)+\ell}\right] \left(\frac{r r_k}{a^2}\right)^{\ell} P_\ell(\cos\vartheta_k)}_{\text{Multipole expansion}}$$

Legendre function

Multipole expansion

$$P_0(x) = 1 \qquad P_1(x) = x \qquad P_2(x) = (2x^2 - 1)/2$$

$$U = \tfrac{1}{2} \sum_j q_j V(r_j)$$

Environment contribution

$$U = \tfrac{1}{2} \sum_{j=1}^{M} \sum_{k=1}^{M} \frac{q_j q_k}{a} \sum_{\ell=0}^{\infty} \left[\frac{(\ell+1)(1-\varepsilon)}{\varepsilon(\ell+1)+\ell}\right] \left(\frac{r_j r_k}{a^2}\right)^{\ell} P_\ell(\cos\vartheta_{jk})$$

$$\vartheta_{jk} = \angle r_j r_k$$

Definite contributions

$$U = \tfrac{1}{2}\sum_{k=1}^{M}\sum_{j=1}^{M}\left(\frac{q_k q_j}{a}\right)\left(\frac{1-\varepsilon}{\varepsilon}+\frac{2(1-\varepsilon)}{2\varepsilon+1}\left(\frac{r_j r_k}{a^2}\right)\cos\theta_{kj}+\ldots\right)$$

$\ell = 0$ $$U_0 = -\frac{1}{2}\left(\frac{q^2}{a}\right)\left(1-\frac{1}{\varepsilon}\right)$$ **Born**

$\ell = 1$ $$U_1 = -\frac{\varepsilon-1}{2\varepsilon+1}\left(\frac{\mu^2}{a^3}\right)$$ **Bell (Onsager ?)**

Onsager Theory

$$E_{tot} = E_g + E_s$$

$$E_s = E_e + E_d + E_c$$ Electrostatic, dispersion, cavitation contributions

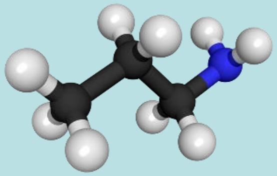
$$U = -\frac{\varepsilon - 1}{2\varepsilon + 1}\left(\frac{\mu^2}{a^3}\right)\left(1 - \frac{\varepsilon - 1}{2\varepsilon + 1}\frac{2\alpha}{a^3}\right)^{-1}$$

$$U = -\frac{\varepsilon - 1}{3\varepsilon + 2}\frac{3}{4a^5}\sum_{i \neq j = 1}^{3}[4\theta_{ii}^2 + 3(\theta_{ij} + \theta_{ji}) - 4\theta_{jj}\theta_{ii}]$$ **Abraham**

$$\theta_{ij} = \sum_k r_{ki}\mu_{kj}$$


John Gamble Kirkwood
1907 — 1959
Physical Chemist
S.B. – University of Chicago (1926);
Ph.D. – Massachusetts Institute of Technology
(1929); S.D. Honoris Causa – University
of Chicago (1954) and Université Libre de
Bruxelles (1959).
Served Yale University as Sterling
Professor of Chemistry, Chairman of the
Chemistry Department (1951 — 1959) and
Director of Division of Sciences (1956 —
1959); Leiden University as Lorentz Professor
of Theoretical Physics (1959); California
Institute of Technology as Noyes Professor
of Chemistry (1947 – 1951); Cornell University
as Todd Professor of Chemistry (1938 – 1947);
National Academy of Sciences as Foreign
Secretary (1954 – 1958); The United States
Government as Scientific Consultant (1941 – 1959).
Scientific Honors: American Chemical
Society Award in Pure Chemistry (1936);
Richards Medal (1950); Lewis Medal (1953).
LARS ONSAGER
1903 — 1976
BORN OSLO, NORWAY
J. WILLARD GIBBS PROFESSOR
NOBEL LAUREATE*
MARGARETHE ONSAGER
1912 — 1991
BORN MARBURG, AUSTRIA
*ETC
K. ASAKA
MIRIAM DING

Multipole contributions into ΔG (кcal/mol) for n-propylamine in water (ε=78)



Spherical shape of cavity		Ellipsoid shape of cavity	
ℓ=1	-0.874	ℓ=1	-1.159
2	-1.075	2	-0.724
3	-0.915	3	-0.107
4	-0.592		
5	-0.378		
6	-0.188		
7	-0.129		
total	**-4.15**	total	**-1.99**

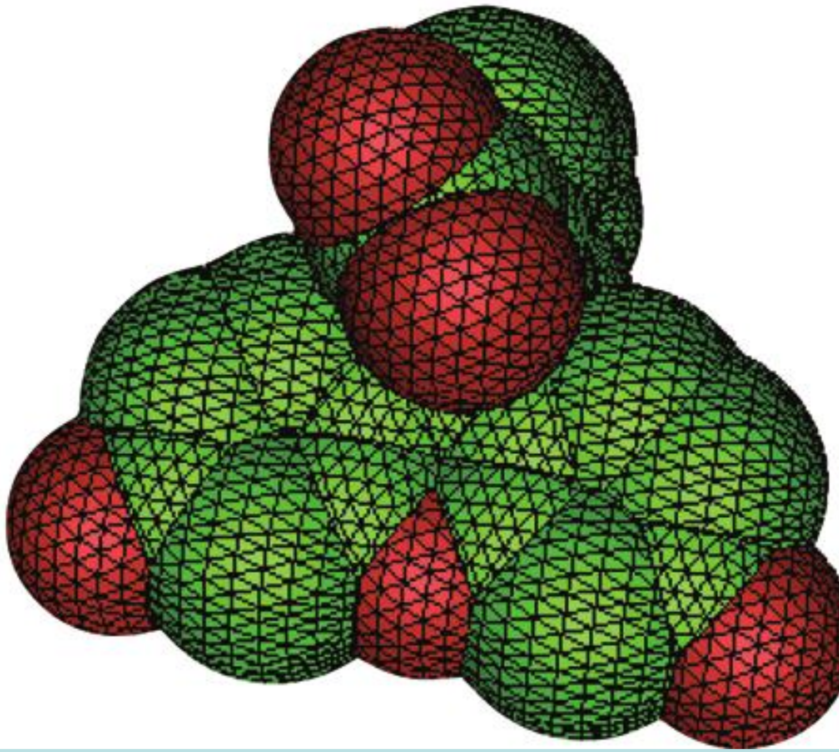
Компонента кубічної π-гіперполяризовності γ(-3ω;ω,ω,ω) (ат. од.) впродовж довгої вісі π-систем у різних середовищах (FCI)

Молекула	ω (в еВ)	Вакуум	Циклогексан	Ацетонітрил	Метанол
Нафталін	0 0.65 1.17	2482 3038 5190	3170 3945 7103	4563 5833 11513	2728 3359 5847
Октатетраєн	0 0.65 1.17	$0.229 \cdot 10^5$ $0.318 \cdot 10^5$ $0.938 \cdot 10^5$	$0.293 \cdot 10^5$ $0.418 \cdot 10^5$ $0.143 \cdot 10^6$	$0.366 \cdot 10^5$ $0.537 \cdot 10^5$ $0.218 \cdot 10^6$	$0.271 \cdot 10^5$ $0.384 \cdot 10^5$ $0.125 \cdot 10^6$
	0 0.65 1.17	$0.205 \cdot 10^5$ $0.294 \cdot 10^5$ - $0.172 \cdot 10^6$	$0.281 \cdot 10^5$ $0.417 \cdot 10^5$ $-0.161 \cdot 10^6$	$0.344 \cdot 10^5$ $0.524 \cdot 10^5$ $-0.152 \cdot 10^6$	$0.243 \cdot 10^5$ $0.355 \cdot 10^5$ - $0.165 \cdot 10^6$

Порівняння сольватохромних зсувів по відношенню до вакууму (Δ, еВ) методів FCI і CIS для найнижчих $\pi\pi^*$– переходів

	Октатетраєн		Нафталін	
Середовище	**ΔCIS**	**ΔFCI**	**ΔCIS**	**ΔFCI**
Циклогексан	0.152	0.150	0.024	0.076
Бензол	0.173	0.173	0.028	0.085
Метанол	0.281	0.284	0.050	0.140
Над поверхнею NaCl	0.110	0.110	0.008	0.031

Формування «реалістичної» порожнини



General solution of electrostatic problem

Methods

1) “Apparent" surface charges
2) Multipole expansion
3) Generalized Born Approximation
4) Finite-difference schemes

$$-\nabla^2 V(r) = 4\pi\rho(r) \quad \text{in cavity}$$

$$-\nabla^2 V(r) = 0 \quad \text{outside cavity}$$

$$V(r) = V_v(r) + V_R(r)$$

$$V_\sigma(\vec{r}) = \int \frac{\sigma(\vec{s})}{|\vec{r} - \vec{s}|} d^2 s \approx \sum_k \frac{\sigma(\vec{s}_k) S_k}{|\vec{r} - \vec{s}_k|}$$

Polarization Continual Model

$$(\mathrm{H} + \mathrm{V}(\Psi))\left|\Psi\right\rangle = \mathrm{E}\left|\Psi\right\rangle$$

Self Consistent Reaction Field (SCRF) – полость - набор перекрывающихся сфер

Static isodensity surface for the cavity (IPCM)

Self-Consistent Isodensity PCM (SCIPCM)

«charge penetration» problem

COSMO (conductor–like screening model)
A. Klamt (1993)

$$U = -\frac{1}{2}\sum_{i,j}\frac{q_i q_j a}{\sqrt{a^4 - 2a^2\vec{r}_i\vec{r}_j + r_i^2 r_j^2}}$$

$$f(\varepsilon) = \frac{\varepsilon - 1}{\varepsilon + k}, \quad k \approx 0.5$$

Implemented in MOPAC, ADF, GAMESS, ORCA

Estimation of accuracy $1/(2\varepsilon)$