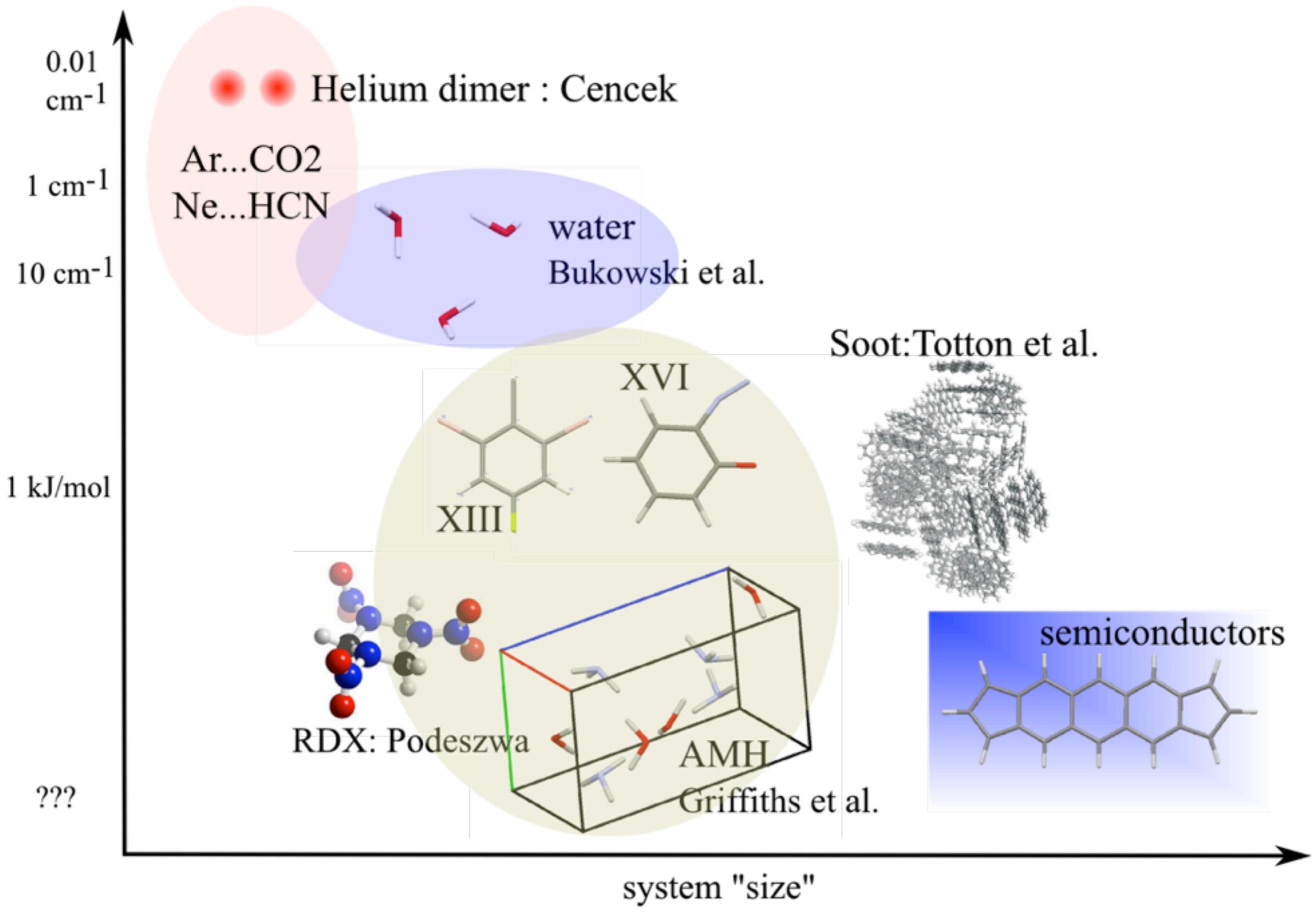


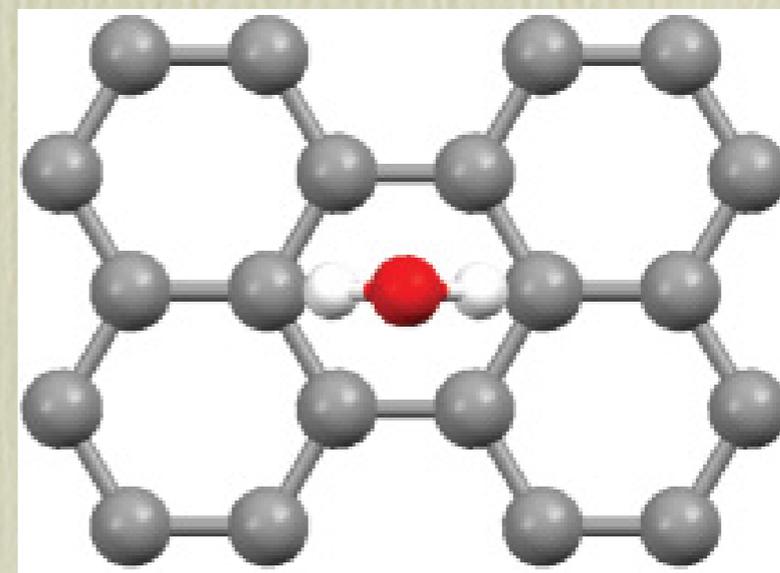
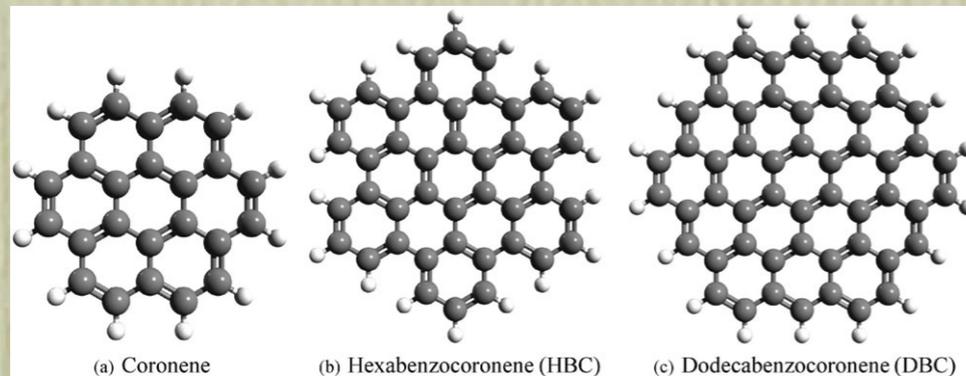
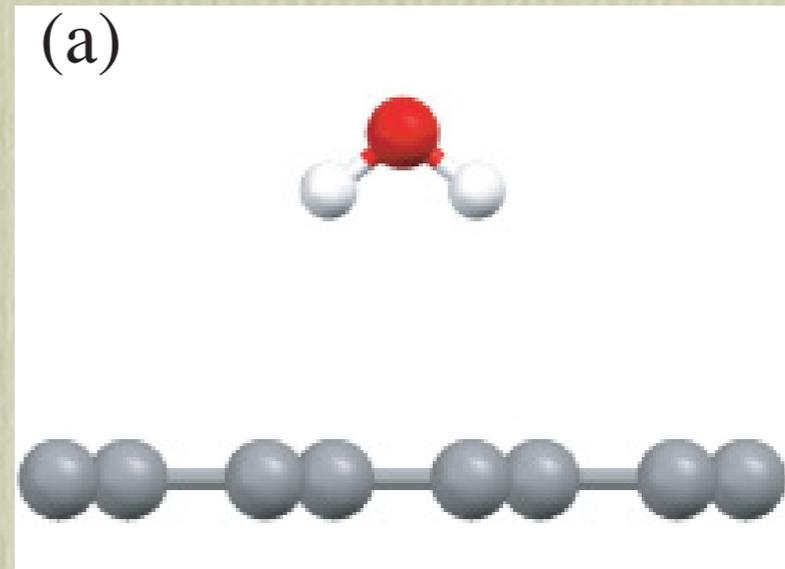
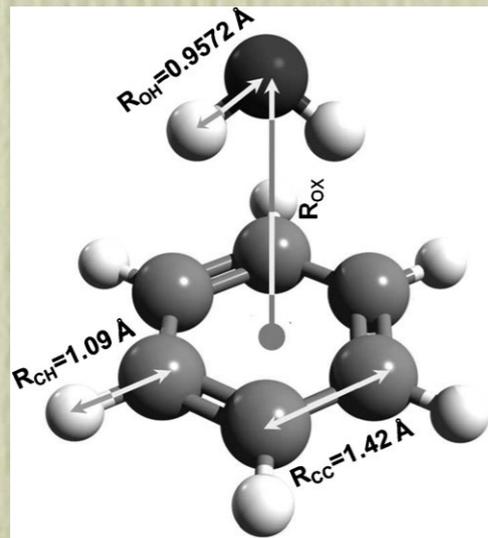
Understanding finite-size effects in molecule-surface adsorption using intermolecular perturbation theory

Alston J. Misquitta





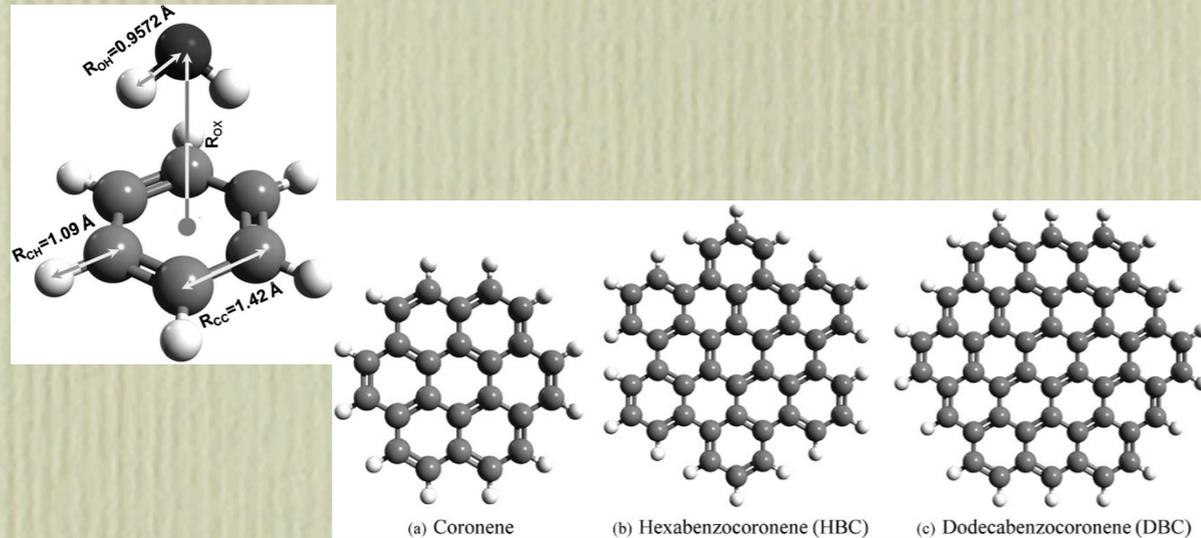
Water on graphene



G. R. Jenness, O. Karalti & K. D. Jordan, PCCP 12 (2010)

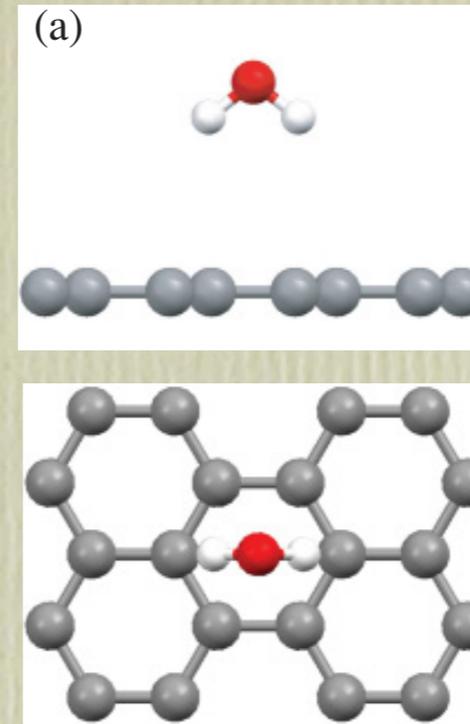
J. Ma, A. Michaelides, D. Alfe, L. Schimka, G. Kresse & E. Wang, PRB 84 (2011)

- Finite systems:



- SAPT(DFT)/DFT-SAPT
- Slow convergence of electrostatic energy
- Binding energy: 130 meV

- Infinite systems



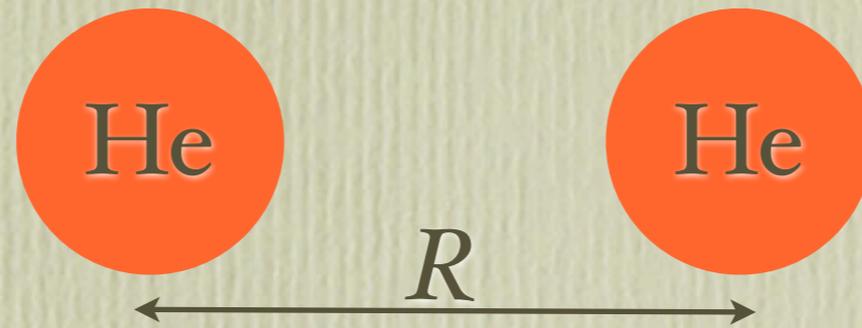
- DMC & RPA
- 14 Angstrom spacing
- DMC 5 x 5: -70(10) meV
- RPA 5 x 5: -77 meV
- RPA 2 x 2/HF 8 x 8: -98 meV

Questions

- Why the 30 meV difference? It's not due to geometry differences.
- What is the nature of the finite-size effects?
- Why were 8 x 8 supercell HF energies needed?
- Which of the two results is more reliable?

Goal of this project is to provide tentative answers to some of these questions. To do this we will use intermolecular perturbation theory.

Perturbation Theory



- Interaction is a small correction:

$$H_{AB} = H_A + H_B + V$$

- Interpretation:

$$\begin{aligned} E_{\text{int}} &= E^{(1)} + E^{(2)} + \dots \\ &= E_{\text{elst}}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{ind}}^{(2)} + E_{\text{disp}}^{(2)} + \dots \end{aligned}$$

SAPT(DFT)

- Express energies in terms of molecular properties

$$E_{\text{elst}}^{(1)} = \int \frac{\rho^A(\mathbf{r}_1)\rho^B(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

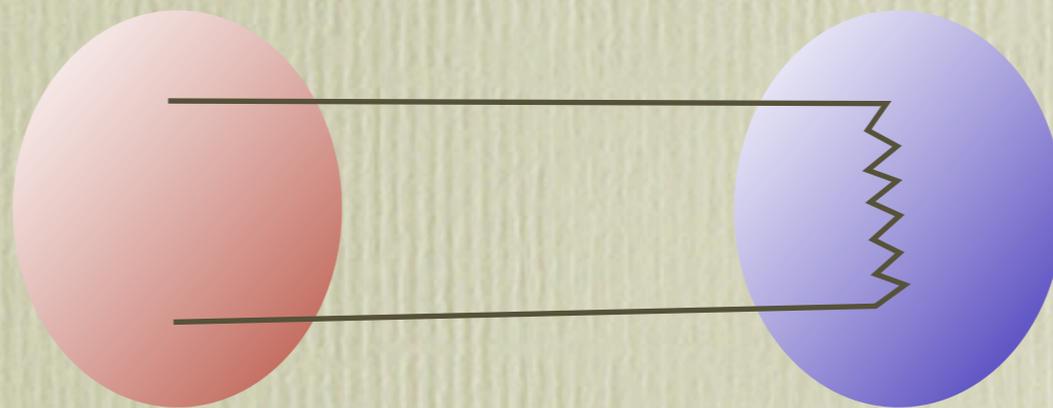
- Un-perturbed densities.

SAPT(DFT)

- Express energies in terms of molecular properties

$$E_{\text{ind}}^{(2)} = -\frac{1}{2} \iint V(\mathbf{r}) \alpha(\mathbf{r}, \mathbf{r}'; 0) V(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

Magnasco & McWeeny (1991)
Angyan *et al* (1994)



- Un-perturbed densities & static density response functions

SAPT(DFT)

- Express energies in terms of molecular properties

$$E_{\text{disp}}^{(2)} = -\frac{1}{2\pi} \int_0^\infty du \iiint \frac{\alpha^A(\mathbf{r}_1, \mathbf{r}'_1; iu) \alpha^B(\mathbf{r}_2, \mathbf{r}'_2; iu)}{|\mathbf{r}_1 - \mathbf{r}_2| |\mathbf{r}'_1 - \mathbf{r}'_2|} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}'_1 d\mathbf{r}'_2$$

Longuet-Higgins (1965)



- Frequency-dependent density response functions

SAPT(DFT)

- Exchange terms: explicitly orbital dependent.
- Terms higher than second-order: mainly induction. Calculated using a combination of HF and SAPT(CHF). Large in polar systems.

SAPT(DFT)

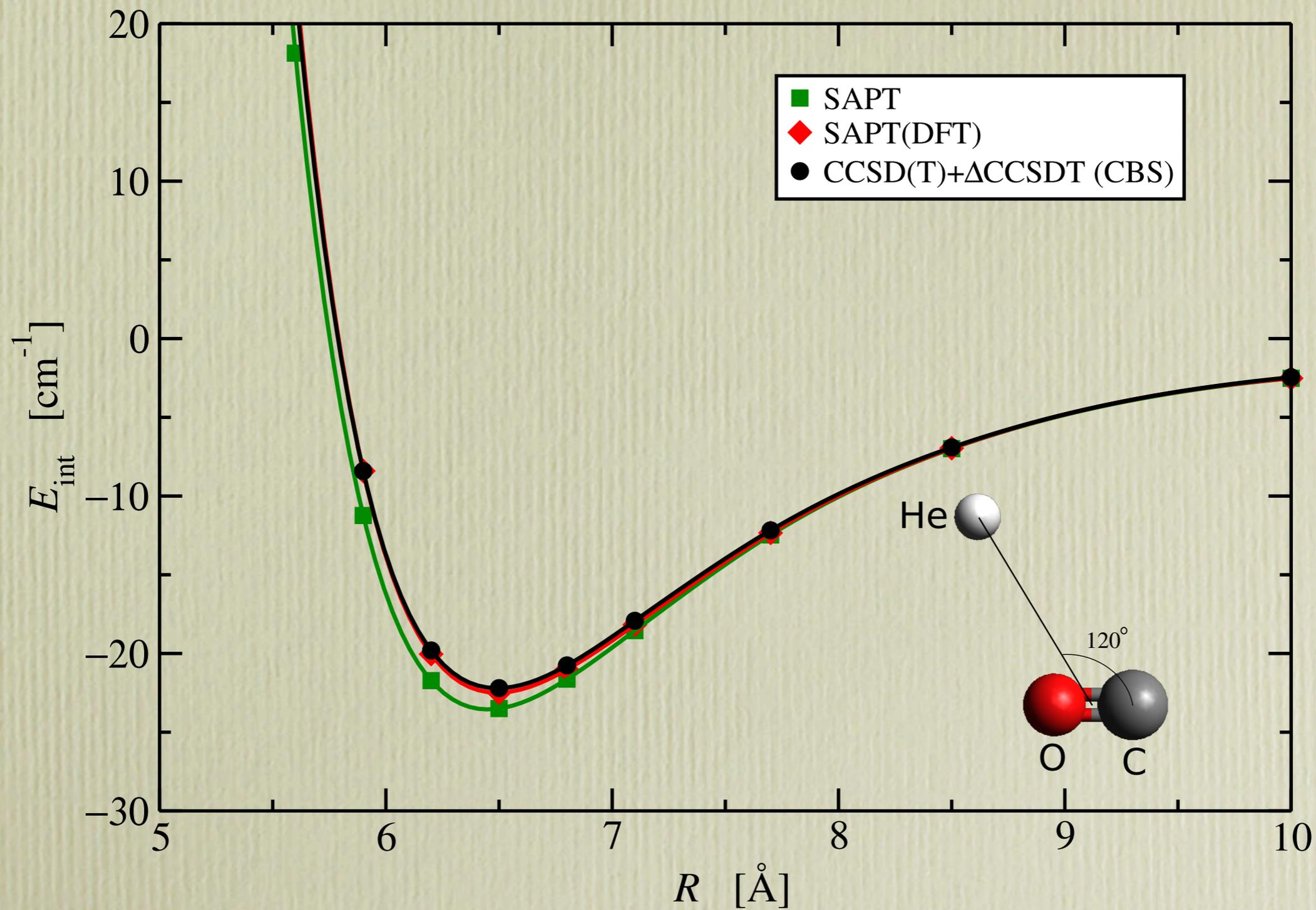
- Molecular properties from DFT & TDDFT
- PBE₀/AC with ALDA+CHF response kernel
- **Density-fitting**: Computational scaling $O(N^5)$
- Accuracy on par with CCSD(T)
- Availability: Molpro, SAPT2008, **CamCASP**
- DFT-SAPT: Hesselmann & Jansen

Misquitta, Jeziorski & Szalewicz, PRL 2003

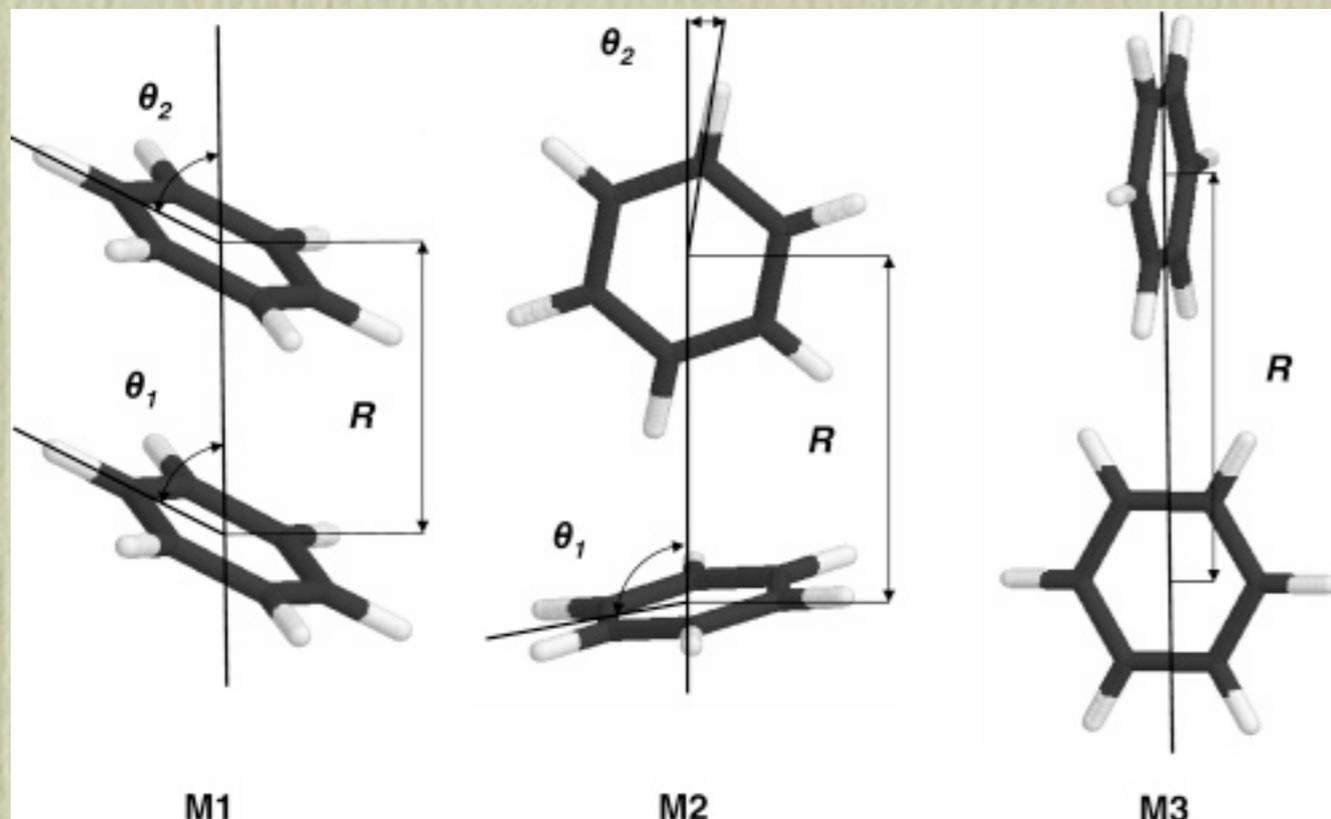
Misquitta & Szalewicz, JCP 2005

Misquitta, Podaszwa, Jeziorski & Szalewicz, JCP 2006

SAPT(DFT) : Accuracy



CCSDT: Peterson; SAPT(DFT): Misquitta, Springer (2012)



energies in meV

<i>Min</i>	<i>SAPT(DFT)</i>	<i>CCSD(T)</i>
M _I	-28.419	-27.973
M ₂	-28.719	-28.968
M ₃	-18.822	-18.708

R. Podeszwa, R. Bukowski & K. Szalewicz, JPC A 110 (2006)

SAPT(DFT)
is very accurate!

water...benzene

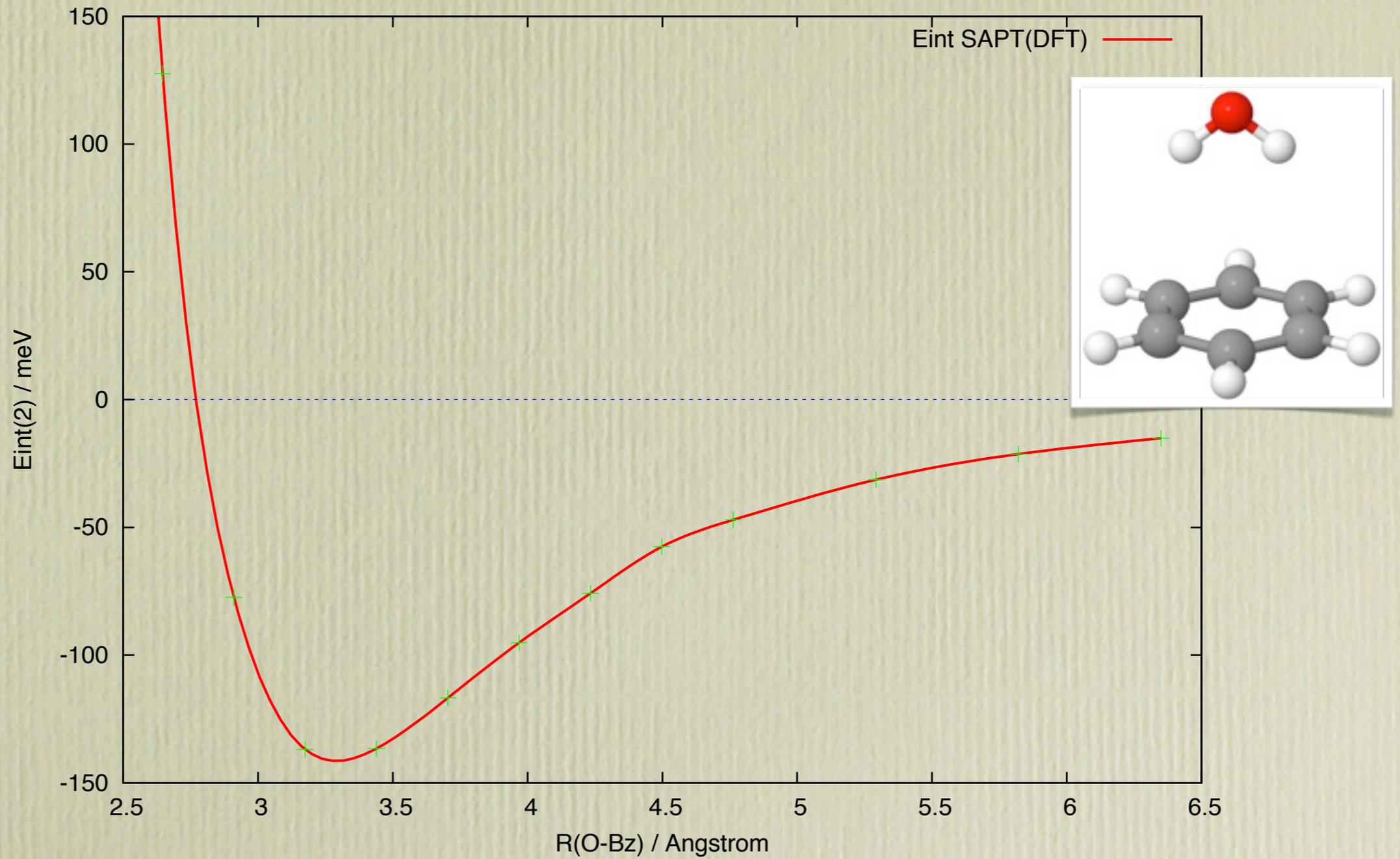
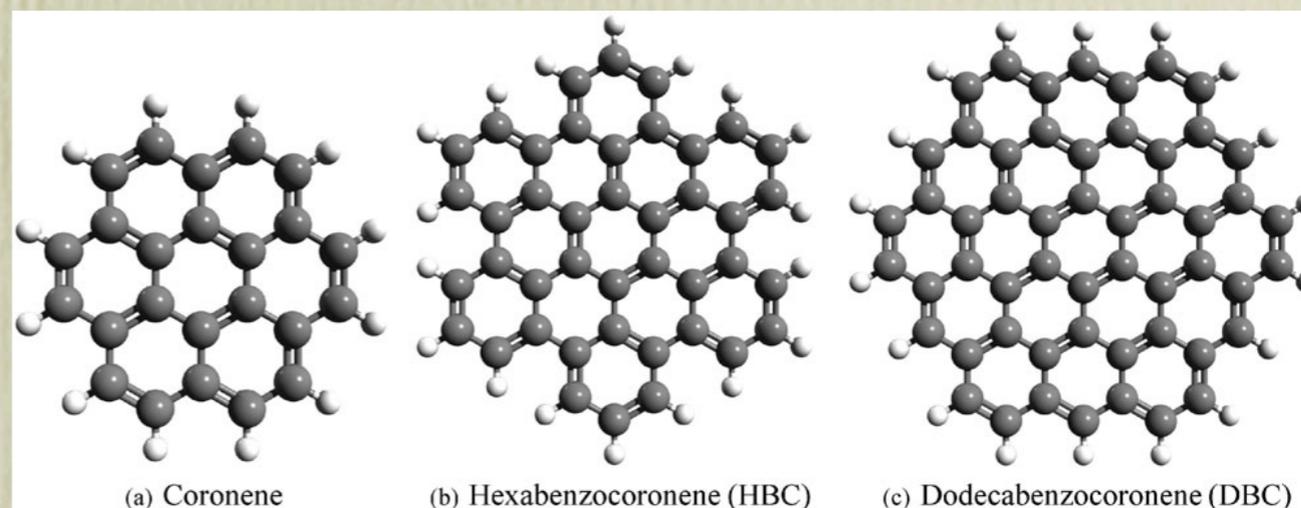
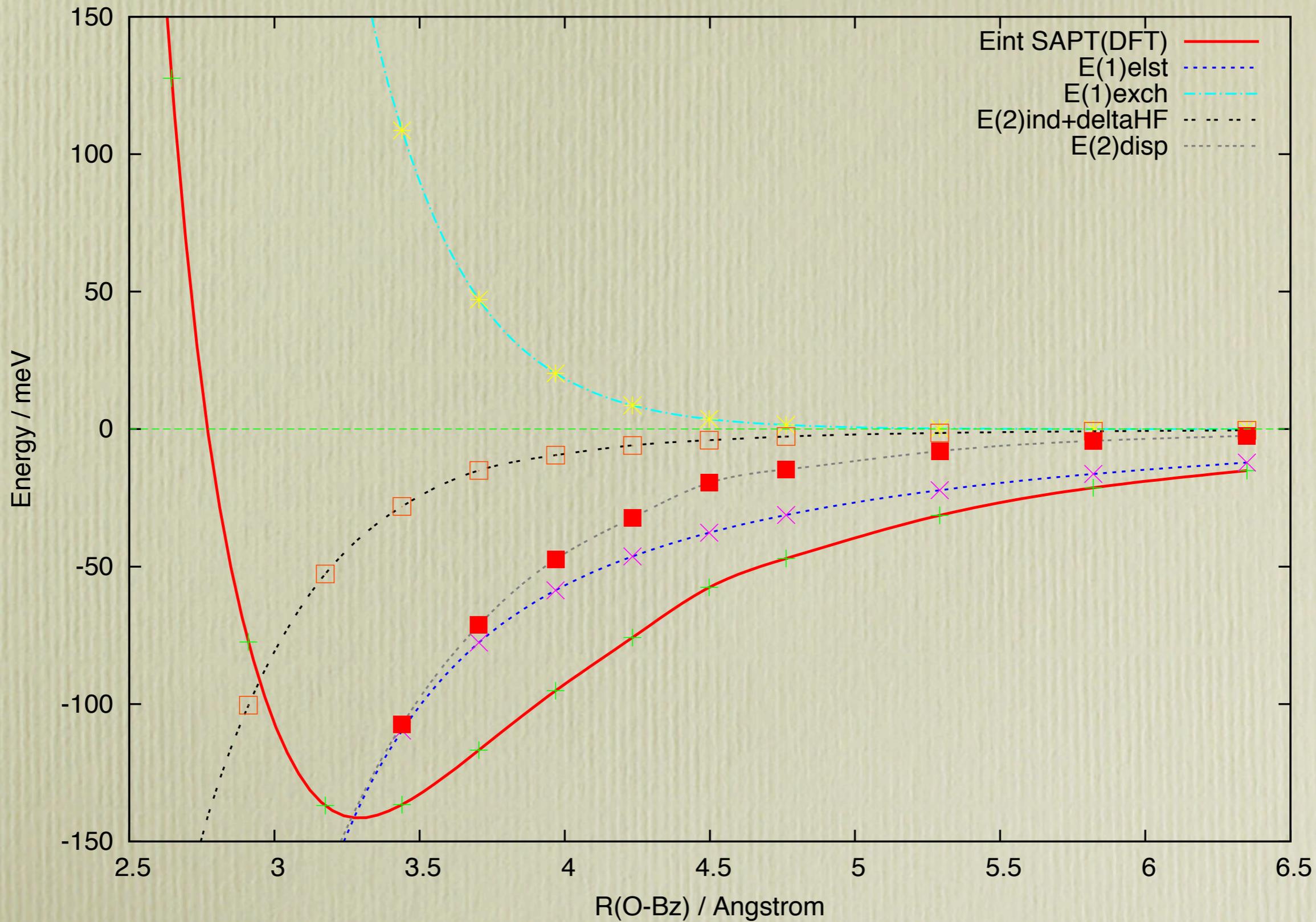


Table 2 Contributions to the DF–DFT–SAPT water–acene interaction energies (kcal mol^{−1})

Term	Benzene	Coronene	HBC	DBC
Electrostatics	−2.85	−1.73	−1.54	−1.39
Exchange–repulsion	3.24	2.79	2.85	2.85
Induction	−1.28	−1.29	−1.36	−1.37
Exchange–induction	0.82	0.80	0.83	0.84
$\delta(HF)$	−0.26	−0.20	−0.23	−0.23
Net induction	−0.71	−0.69	−0.75	−0.75
Dispersion	−3.28	−3.83	−4.00	(−4.07) ^a
Exchange–dispersion	0.44	0.42	0.43	(0.43)
Net dispersion	−2.84	−3.42	−3.57	(−3.64) ^a
Total interaction energy	−3.16	−3.05	−3.01	(−2.93) ^b





Electrostatics

- Involves un-perturbed charge densities of monomers.
- **Finite system**: large source of error. Slow to converge with system size.
- **Periodic system**: Introduces constant repulsive term of water with periodic images. Not a problem.

Dispersion

- **Finite-system**: Slow to converge, but easy to correct for finite-size using $-C_6/R^6$ terms. Potentially missing terms from long wavelength fluctuations in graphene.
- **Periodic system**: Constant repulsive dispersion between water and periodic images(!). Long wavelength terms missing. Spurious attraction from periodic images in graphene.

Induction

- Graphene polarizes water. Distance-dependent.
- Water polarizes graphene. Distance-dependent.
- Water 'sees' image in graphene. Second-order polarization. Distance-dependent.
- Charge transfer!
- **Finite system**: No problem. Converges quickly.
- **Periodic system**: Spurious distance-dependent interactions between water and periodic images.

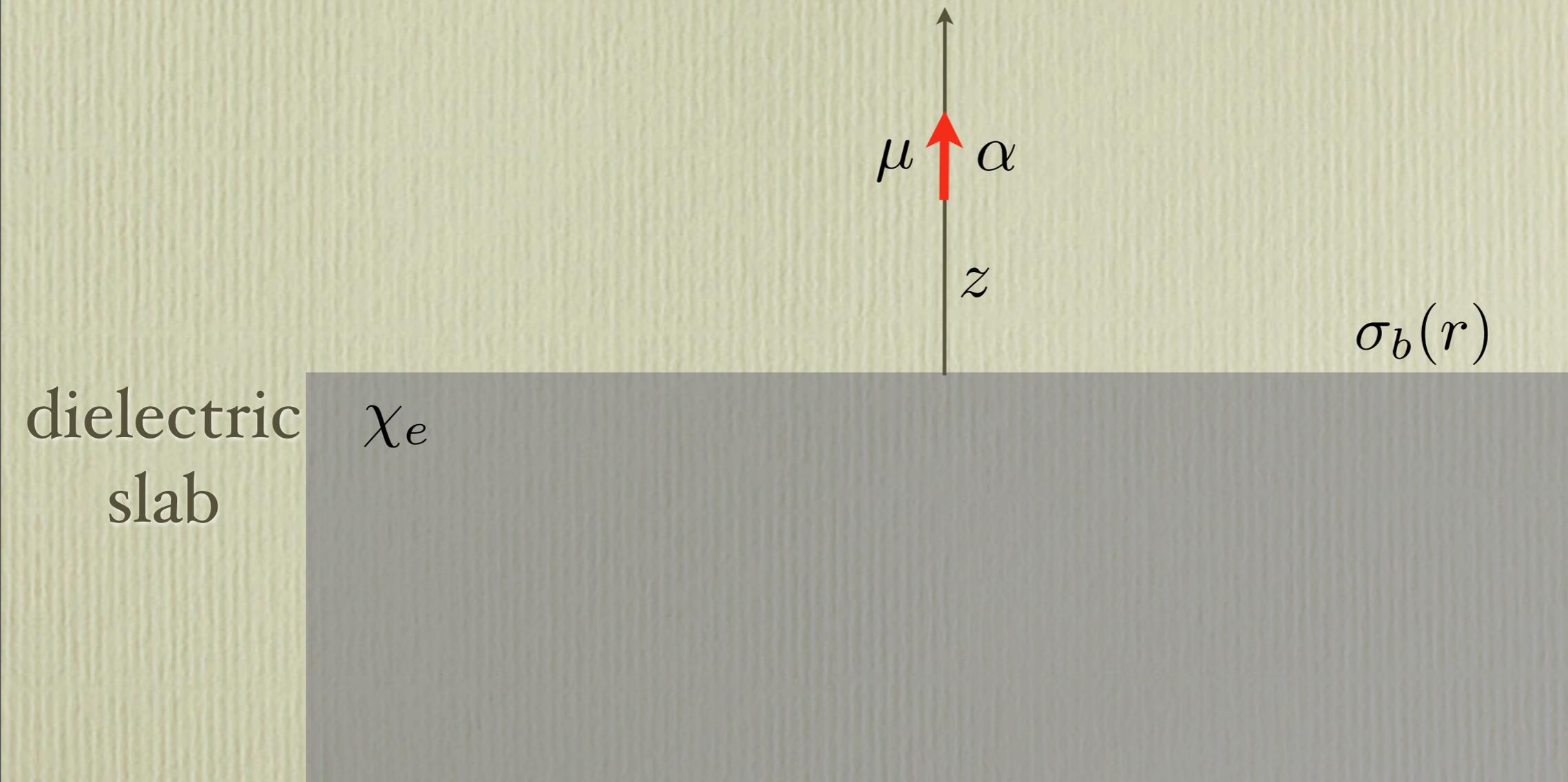
Γ -D periodic model system



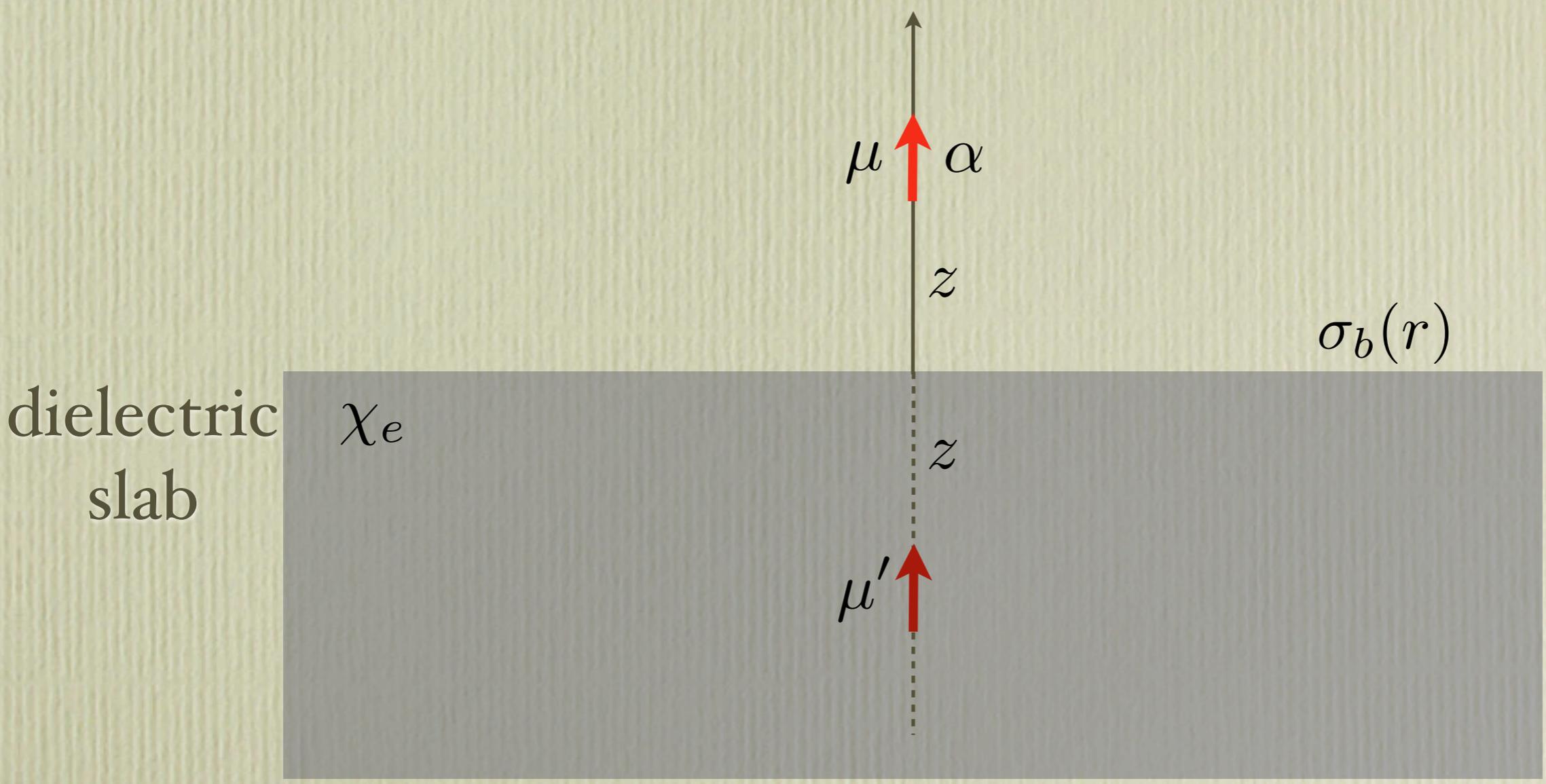
dielectric
slab

χ_e

Γ -D periodic model system

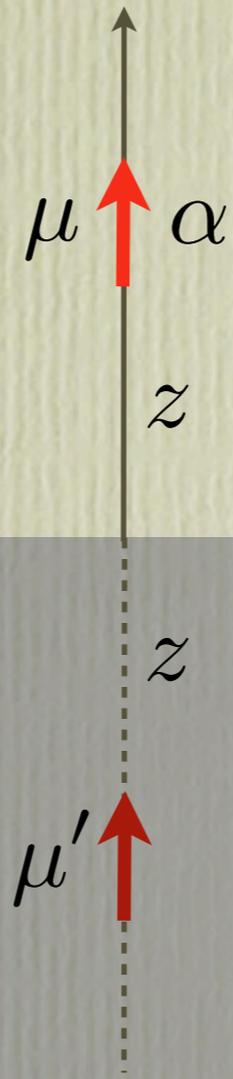


Γ -D periodic model system



r-D periodic model system

$$\mu' = \mu \left(\frac{\chi_e}{\chi_e + 2} \right)$$



$\sigma_b(r)$

dielectric
slab

χ_e

μ'

True induction energy

- Induced dipole: $\Delta\mu = \alpha\bar{E}$

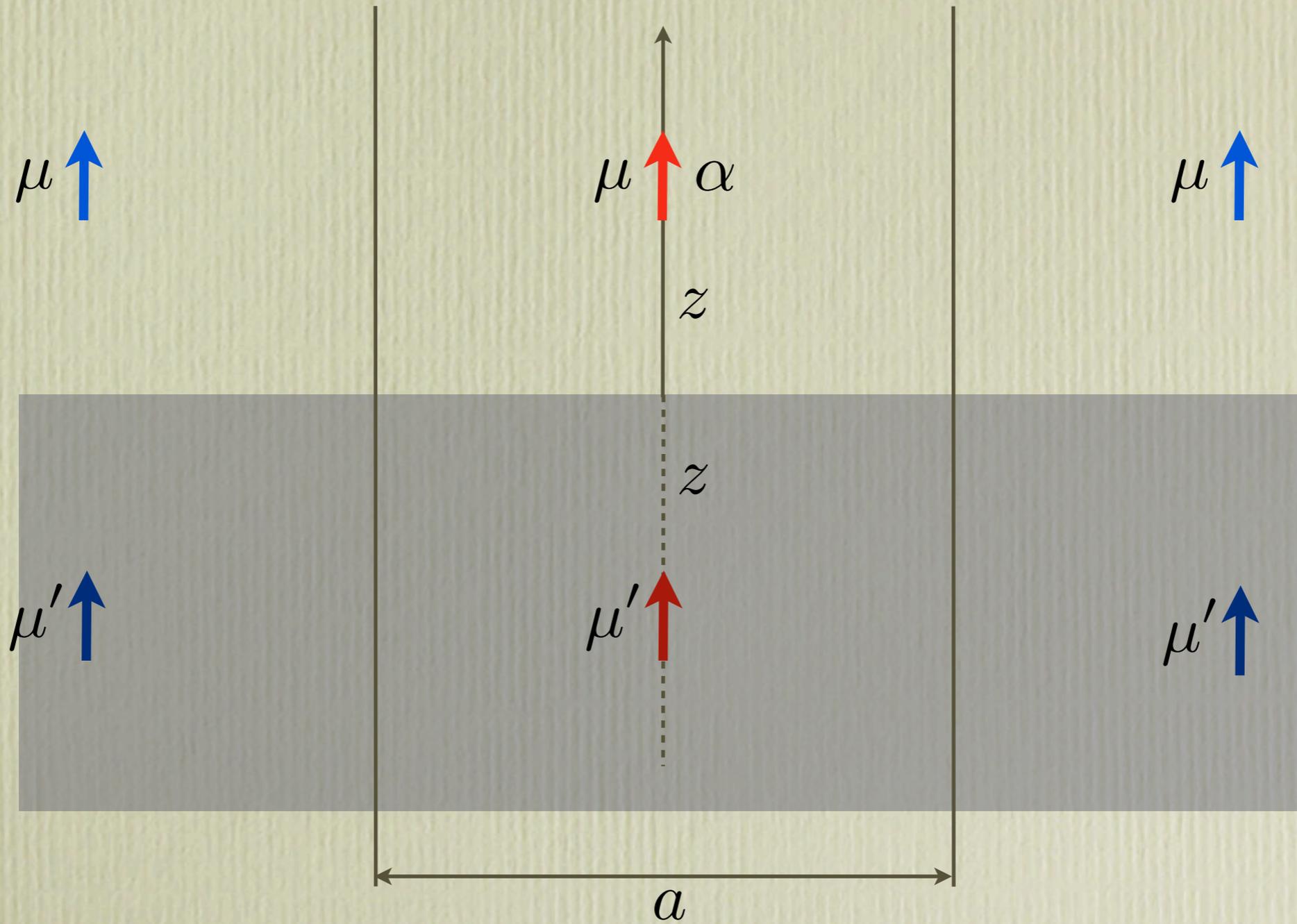
$$= \frac{1}{4\pi\epsilon_0} \frac{\alpha\mu'}{4z^3} \hat{z}$$

- Induction energy:

$$\begin{aligned} E_{\text{ind}} &= -\frac{1}{2} \Delta\bar{\mu}\bar{E} \\ &= -\left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{\alpha\mu^2}{32} \left(\frac{\chi_e}{\chi_e + 2}\right)^2 \frac{1}{z^6} \end{aligned}$$

- This is the true induction (in this model!).

Periodic in r -D



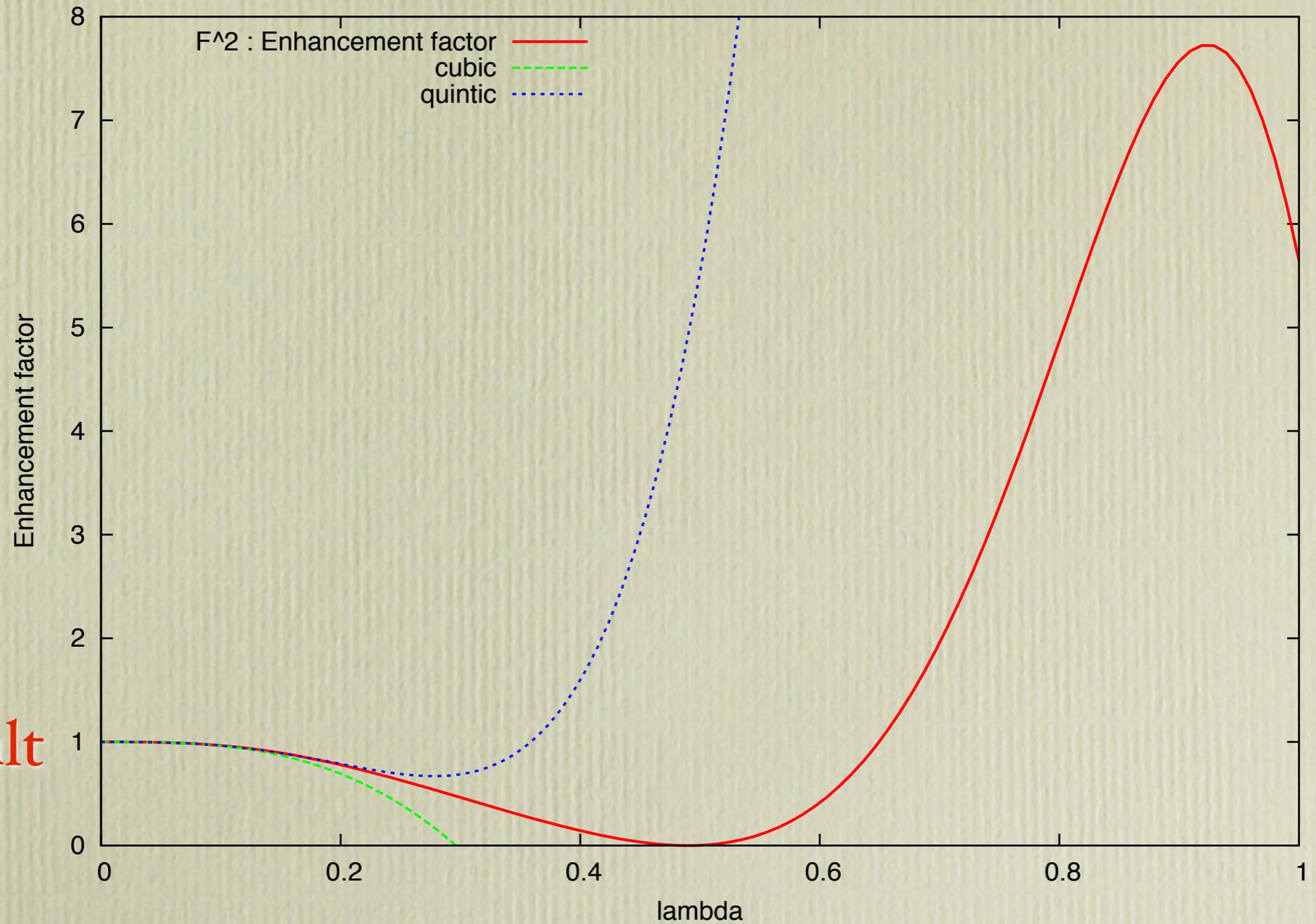
- Define: $\lambda = \frac{z}{a}$
- Field arises from images in the dielectric and due to periodic boundary conditions (PBCs).

$$\begin{aligned}\bar{E} &= \frac{1}{4\pi\epsilon_0} \frac{2\bar{\mu}}{8d^3} \left(\frac{\chi_e}{\chi_e + 2} \right) \left[-8\zeta(3)\lambda^3 \left(\frac{\chi_e + 2}{\chi_e} \right) + 1 + \lambda^3 \sum_{n=1}^{\infty} \frac{1}{n^3} \frac{\frac{8\lambda^2}{n^2} - 1}{\left(1 + \frac{4\lambda^2}{n^2}\right)^{5/2}} \right] \\ &= \frac{1}{4\pi\epsilon_0} \frac{2\bar{\mu}}{8d^3} \left(\frac{\chi_e}{\chi_e + 2} \right) [F(\lambda)]\end{aligned}$$

- And the induction energy is:

$$\begin{aligned}E_{\text{ind}} &= -\frac{1}{2} \Delta\bar{\mu} \bar{E} \\ &= - \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{\alpha\mu^2}{32} \left(\frac{\chi_e}{\chi_e + 2} \right)^2 \frac{1}{z^6} [F(\lambda)]^2\end{aligned}$$

$$[F(\lambda)]^2$$

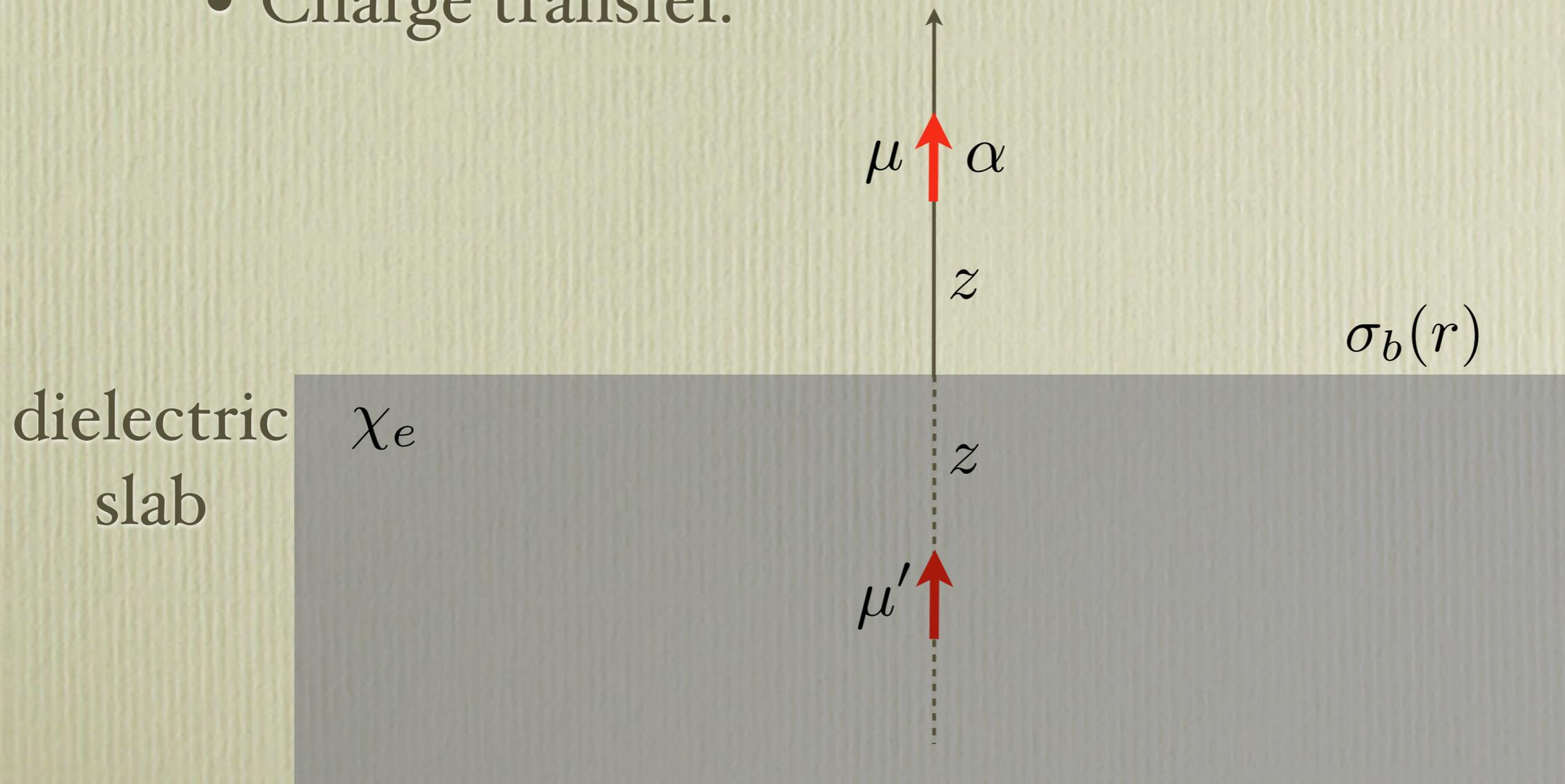


True result

Effects of order 1 meV, so unimportant.

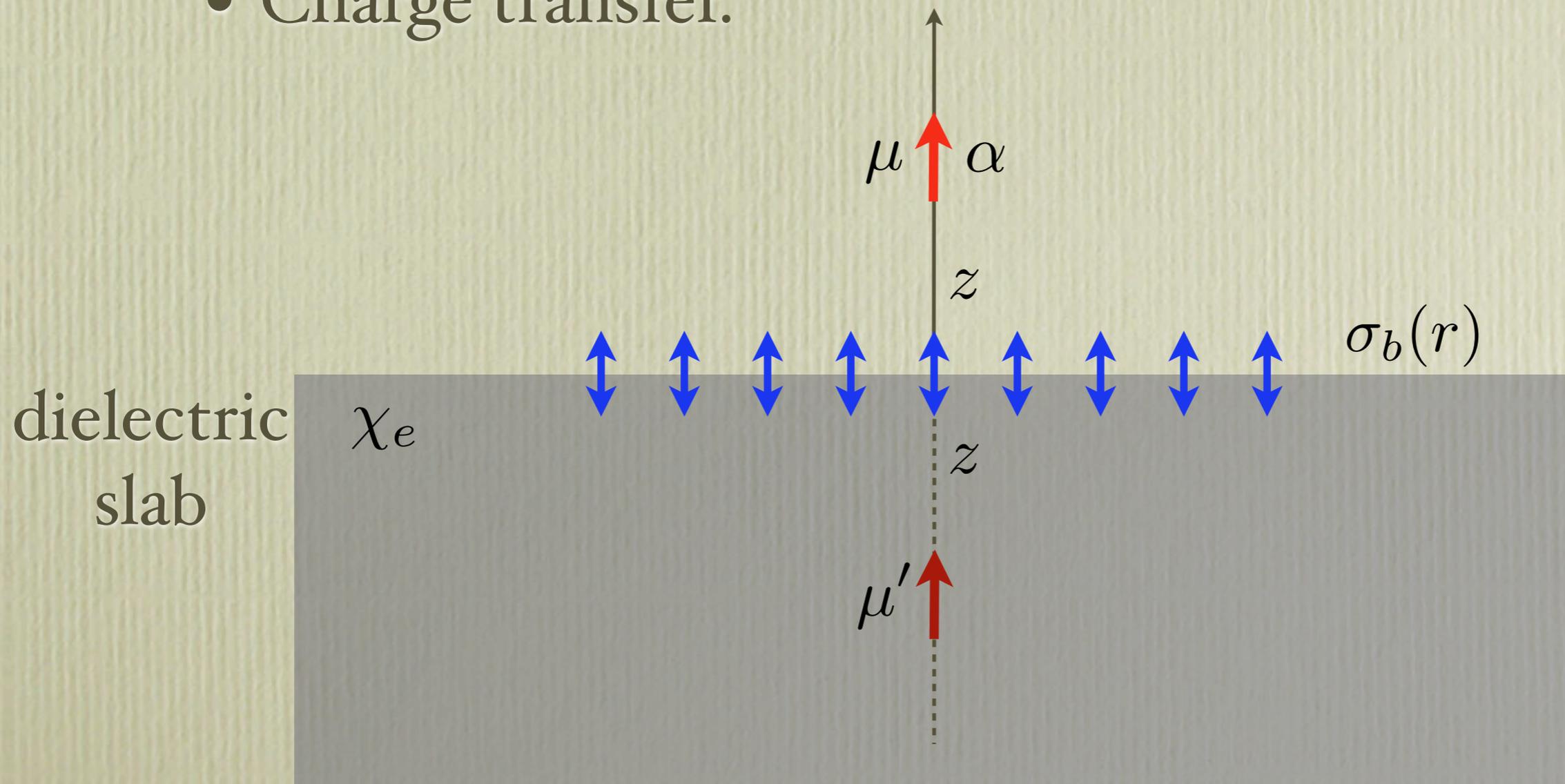
Missing effects

- Polarization from the surface quadrupoles.
- Charge transfer.



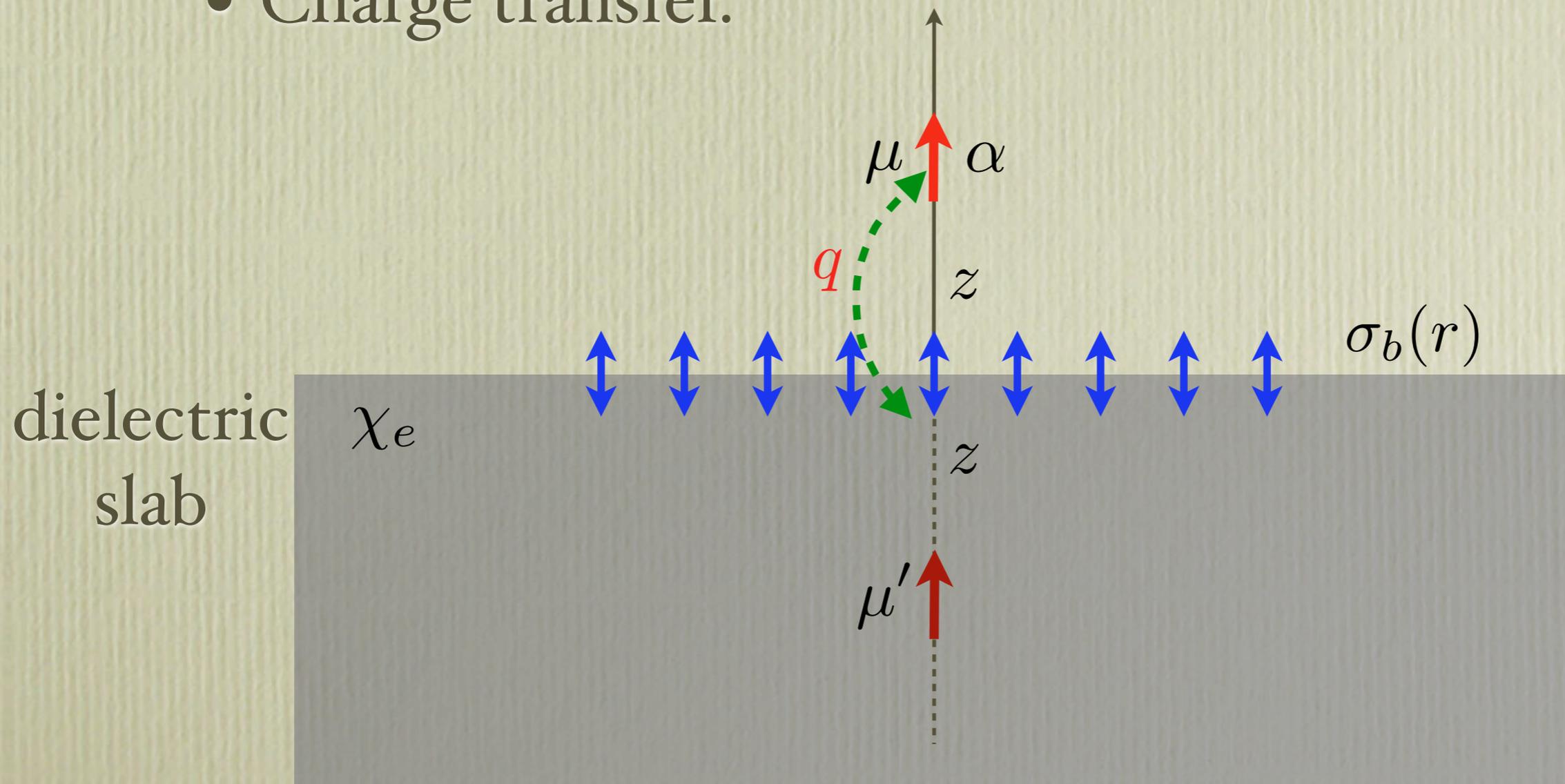
Missing effects

- Polarization from the surface quadrupoles.
- Charge transfer.



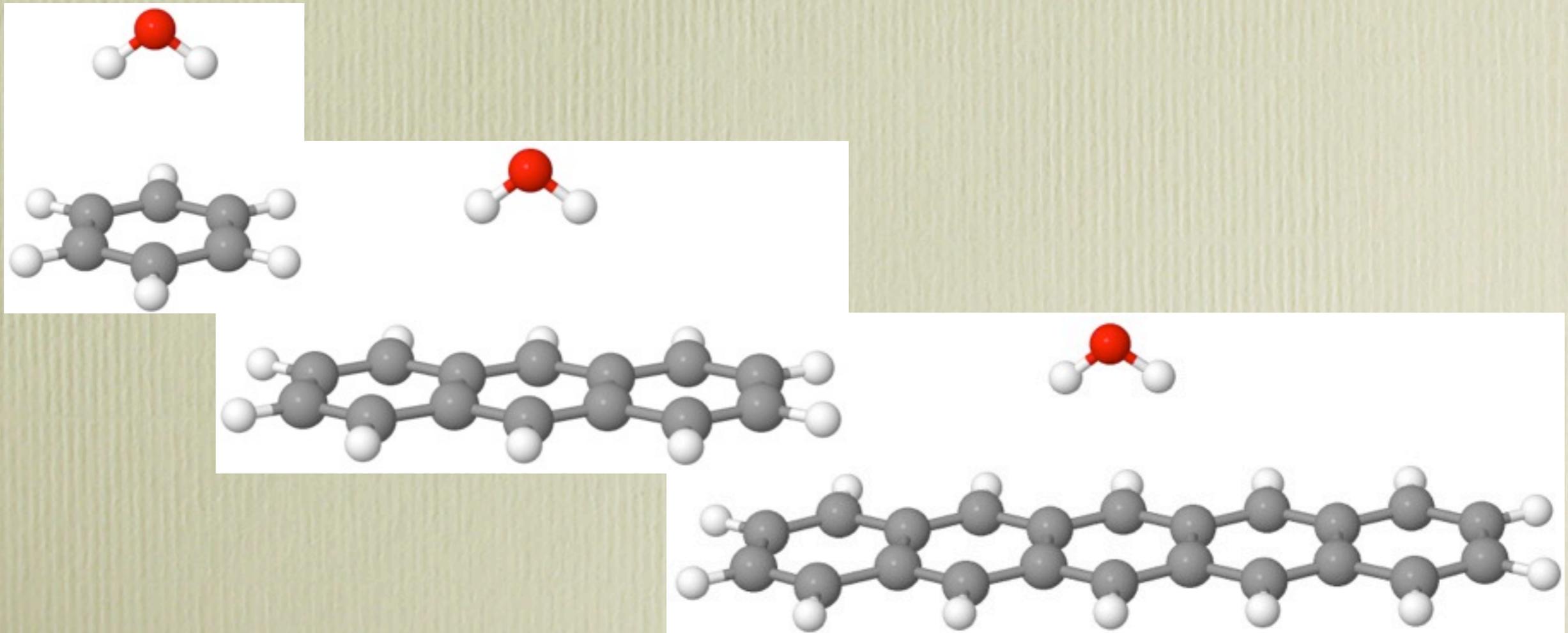
Missing effects

- Polarization from the surface quadrupoles.
- Charge transfer.



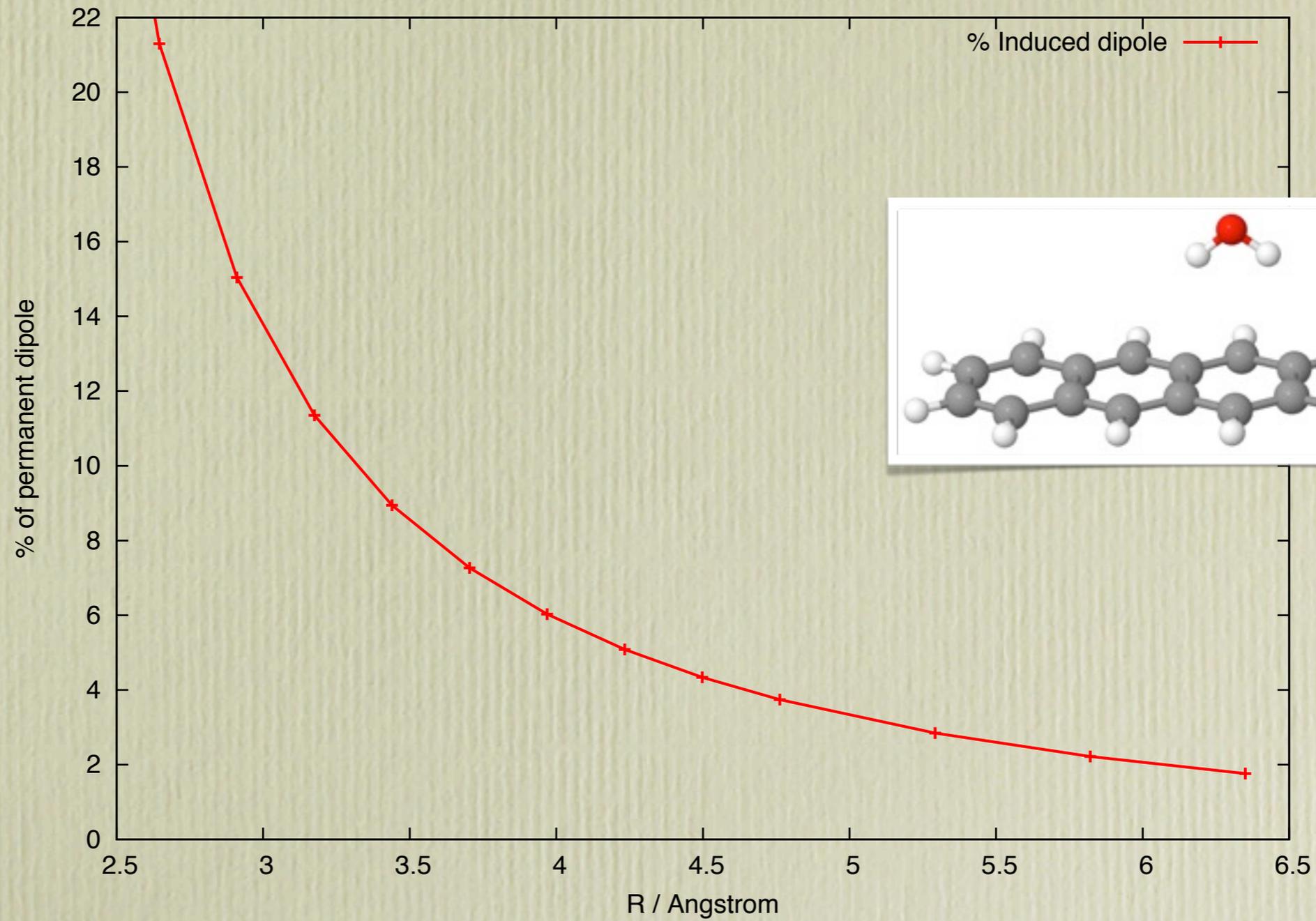
Approach

- Develop an understanding using water...PAH systems.
- Use this information on periodic systems.

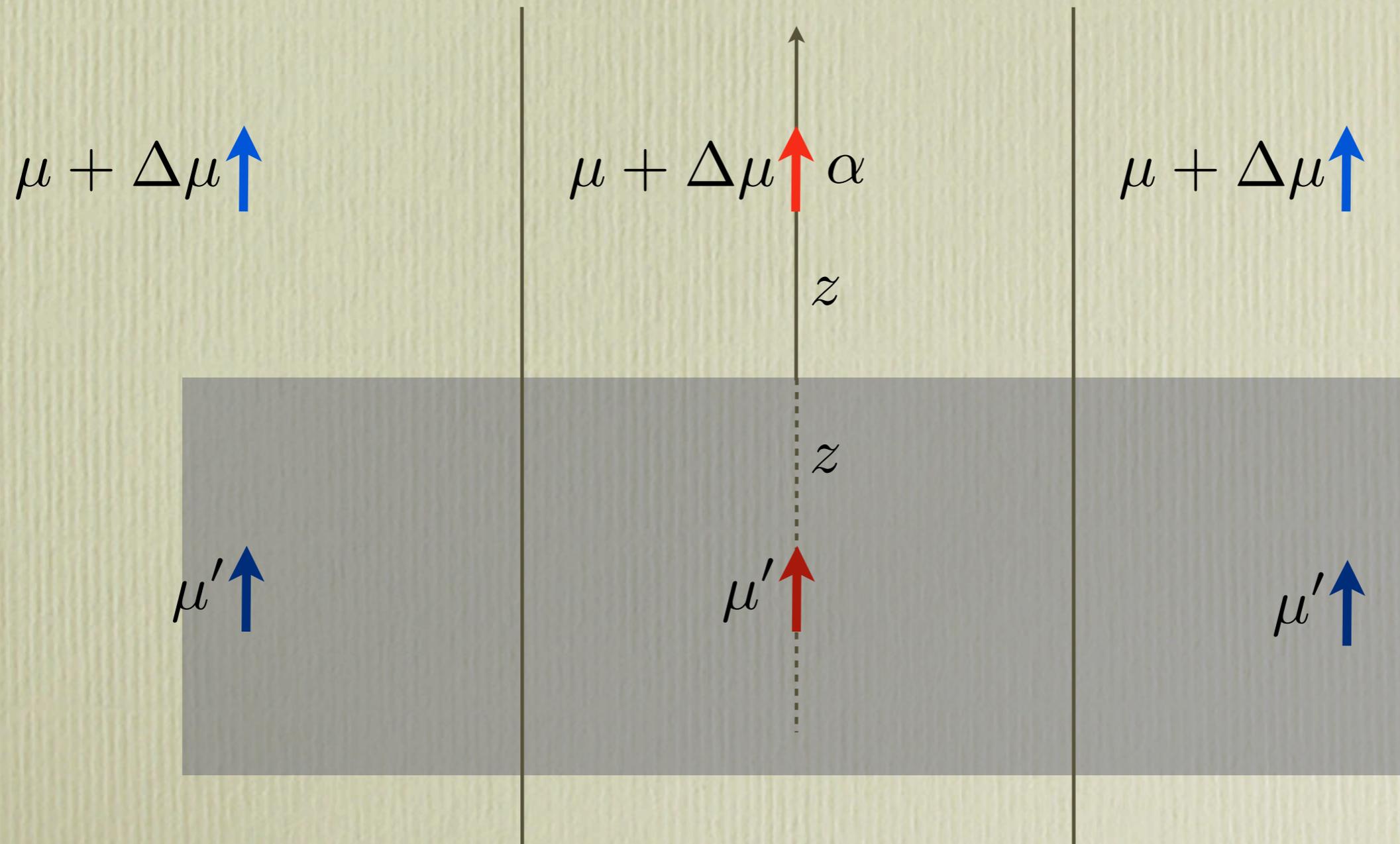


- PBE_o/AC or PBE with Sadlej-pVTZ basis
- Linear-response DFT with ALDAX+CHF or ALDAX kernel.
- Non-local polarizabilities. Ranks 0 to 4 available, but only 0 to 2 used.
- Multipoles from GDMA₂.
- CamCASP and ORIENT.
- Multipoles on PAH replaced with $Q_{20} = -1.161$

water...pentacene

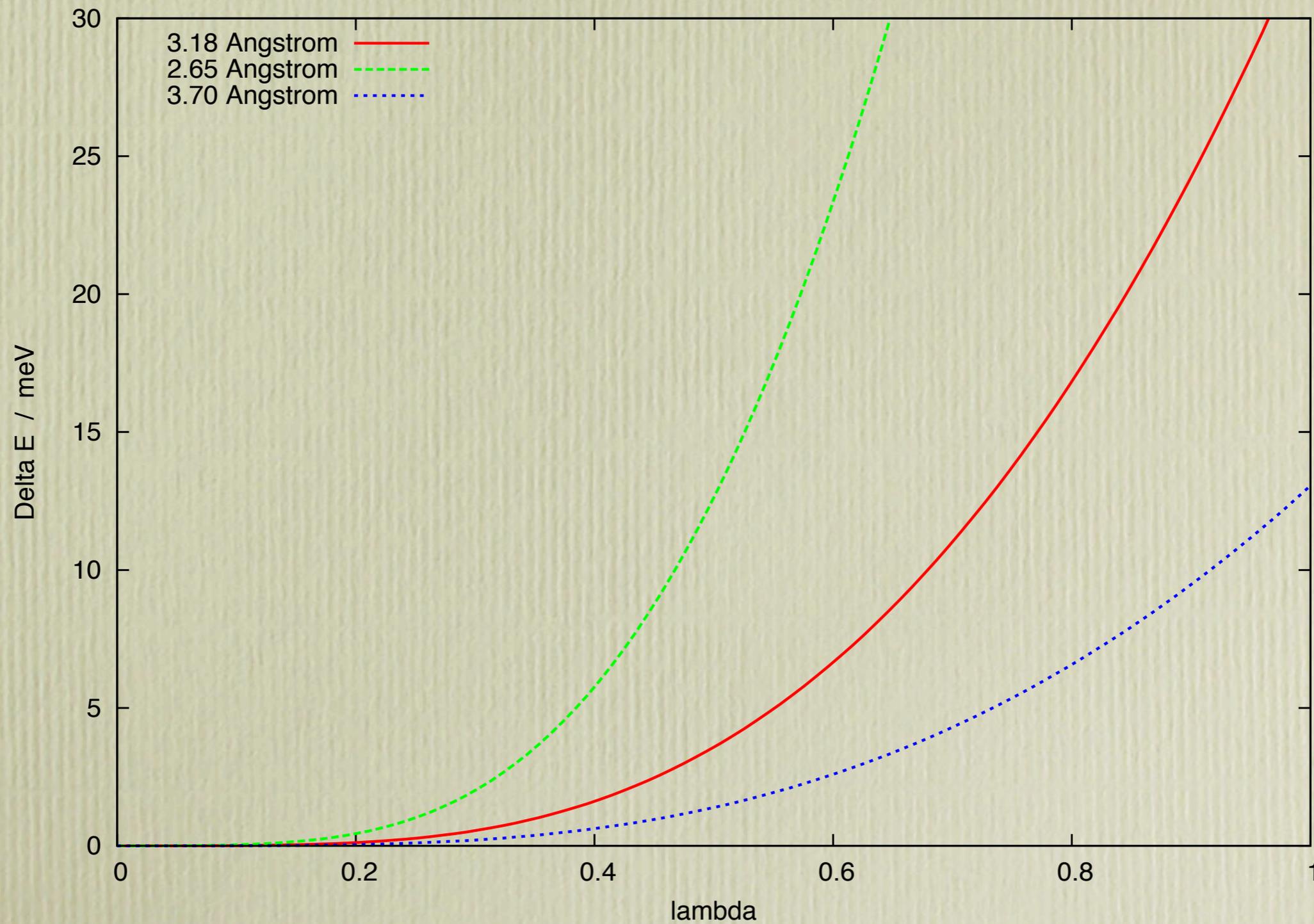


- What is the spurious induction energy resulting from this dipole change?



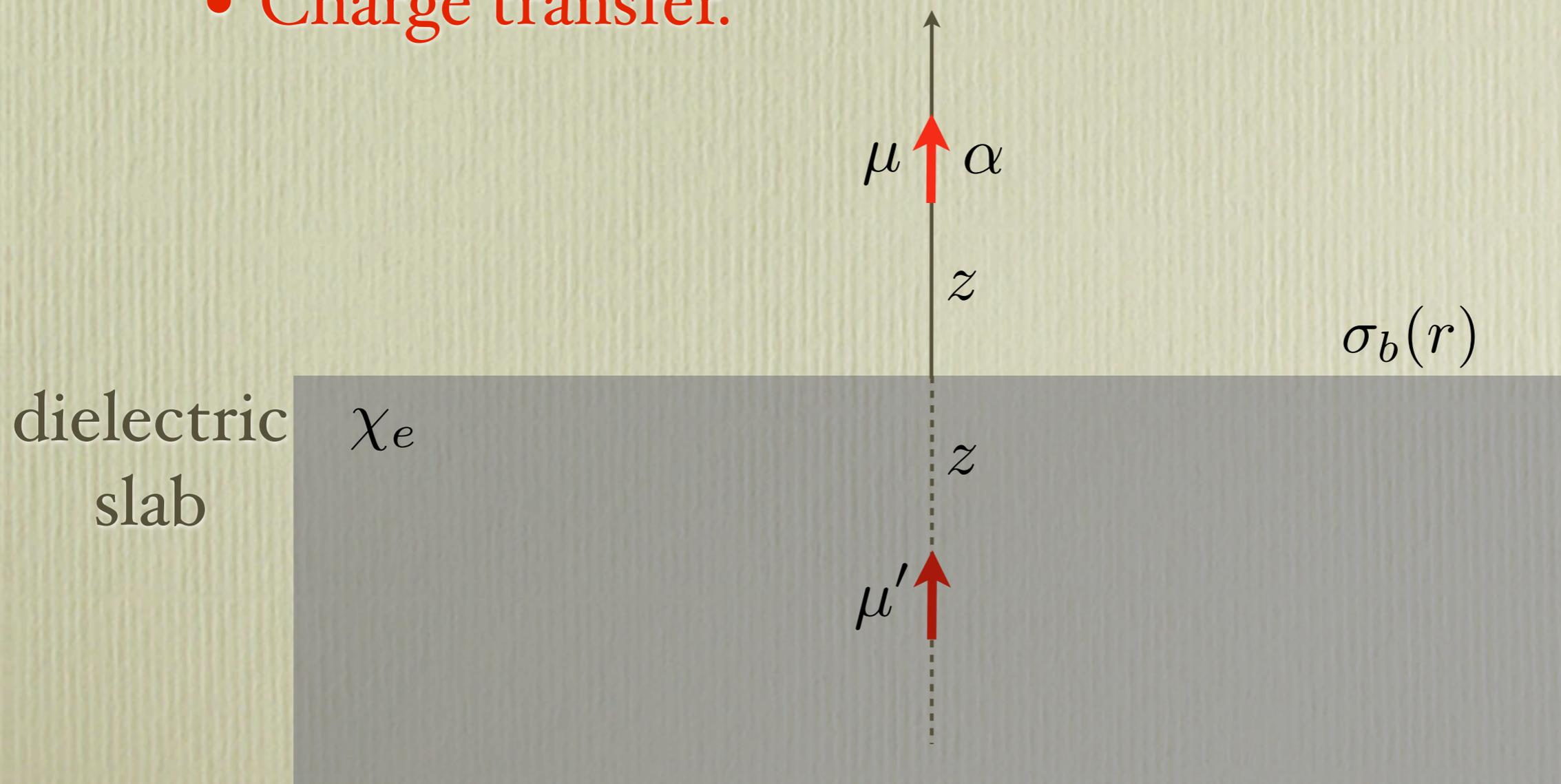
- Field: $\bar{E} = \bar{E}(Q_{20}) + \bar{E}(\mu') + \bar{E}^{\text{PB}}(\mu + \Delta\mu) + \bar{E}^{\text{PB}}(\mu')$
- $E_{\text{ind}} = -\frac{1}{2}\Delta\mu\bar{E}$
 $= -\frac{1}{2}\Delta\mu\bar{E}(Q_{20}) - \frac{1}{2}\Delta\mu\bar{E}(\mu') - \frac{1}{2}\Delta\mu\bar{E}^{\text{PB}}(\mu + \Delta\mu) - \frac{1}{2}\Delta\mu\bar{E}^{\text{PB}}(\mu')$
- Assumes that induced dipole doesn't change in presence of periodic images.
- Square lattice

$$E_{\text{ind}}^{\text{PB}} = -\frac{1}{2}\Delta\mu\bar{E}^{\text{PB}}(\mu + \Delta\mu) - \frac{1}{2}\Delta\mu\bar{E}^{\text{PB}}(\mu')$$



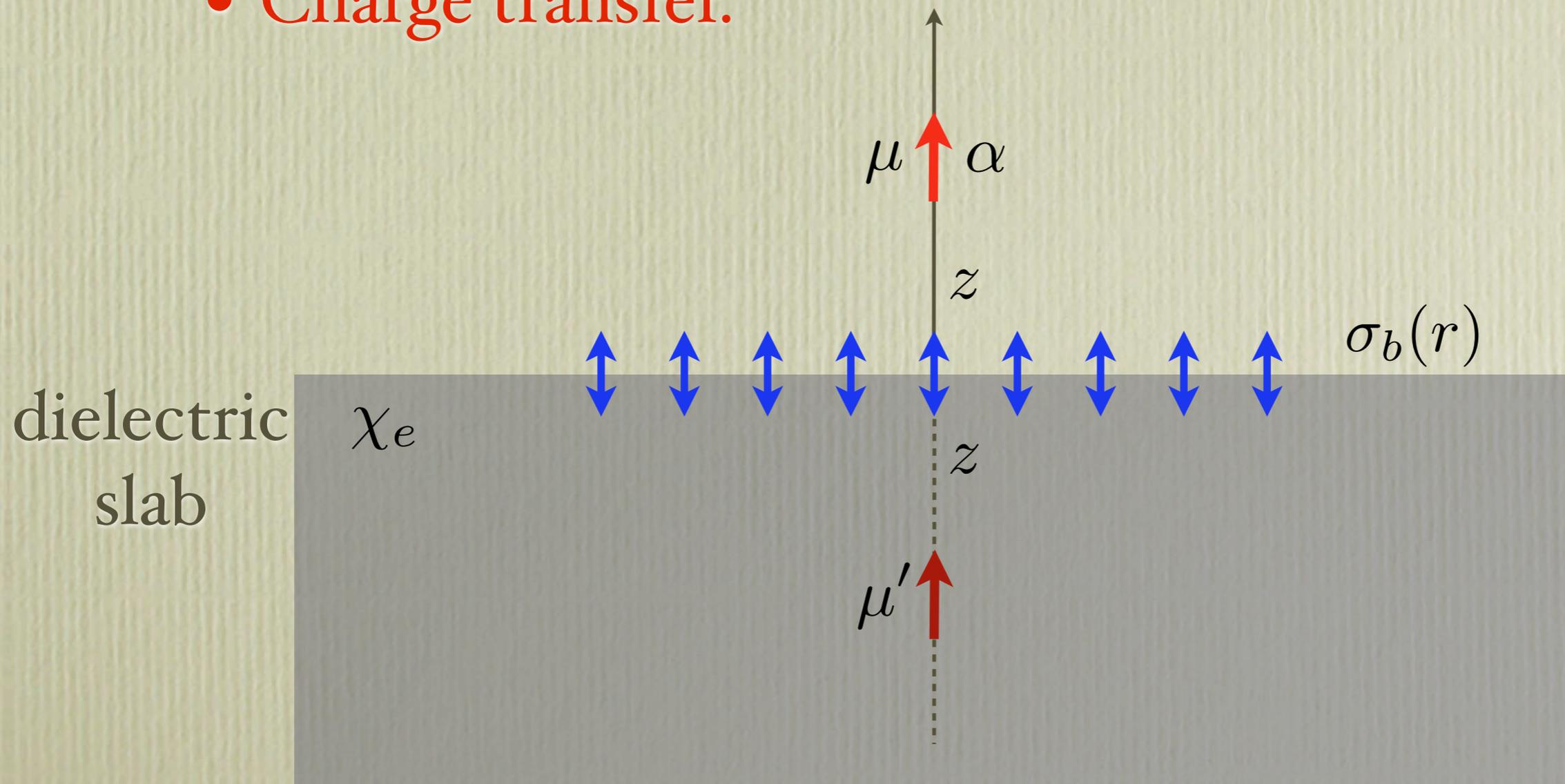
Missing effects

- Polarization from the surface quadrupoles.
- Charge transfer.



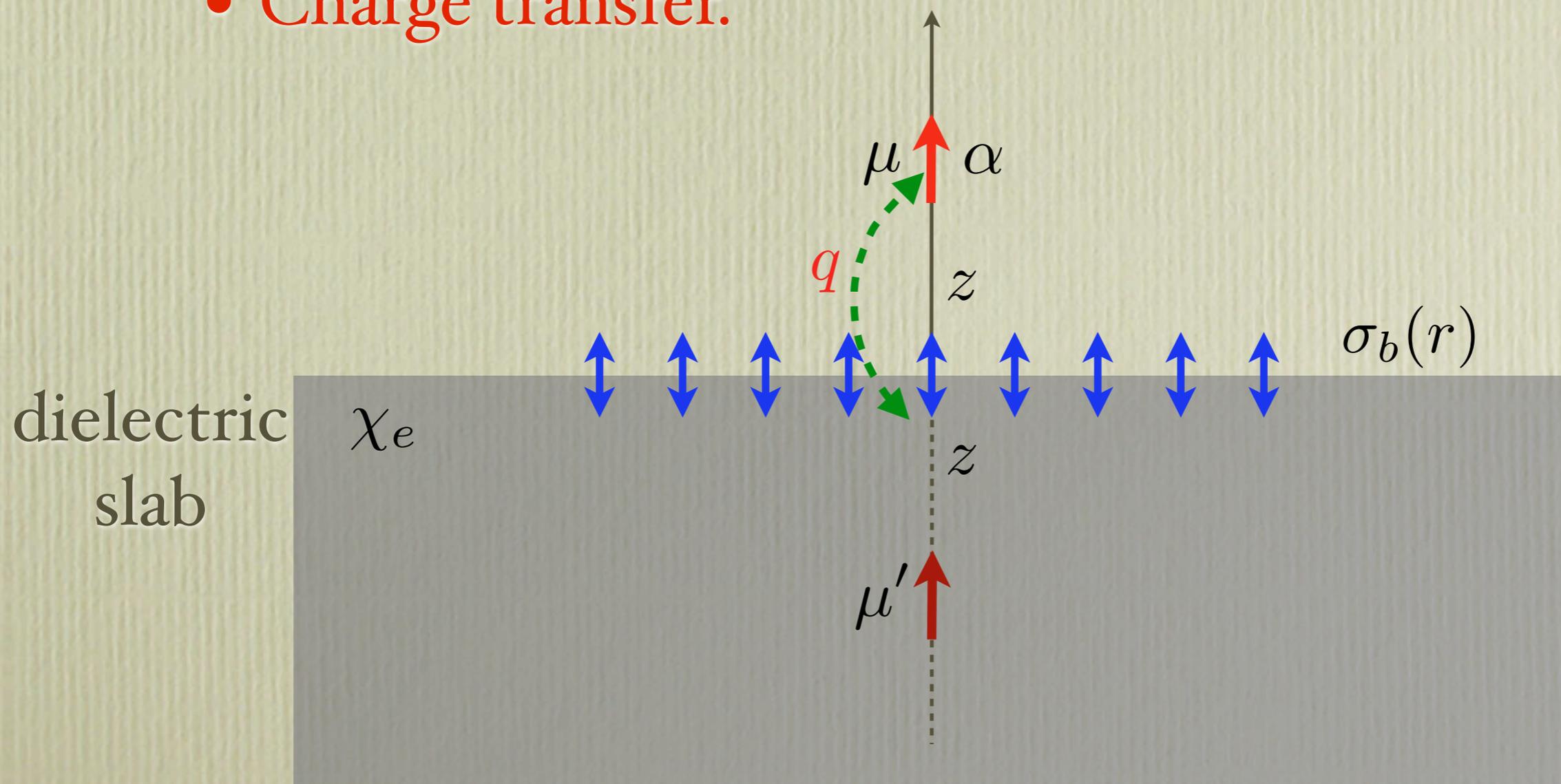
Missing effects

- Polarization from the surface quadrupoles.
- Charge transfer.



Missing effects

- Polarization from the surface quadrupoles.
- Charge transfer.



What is CT?

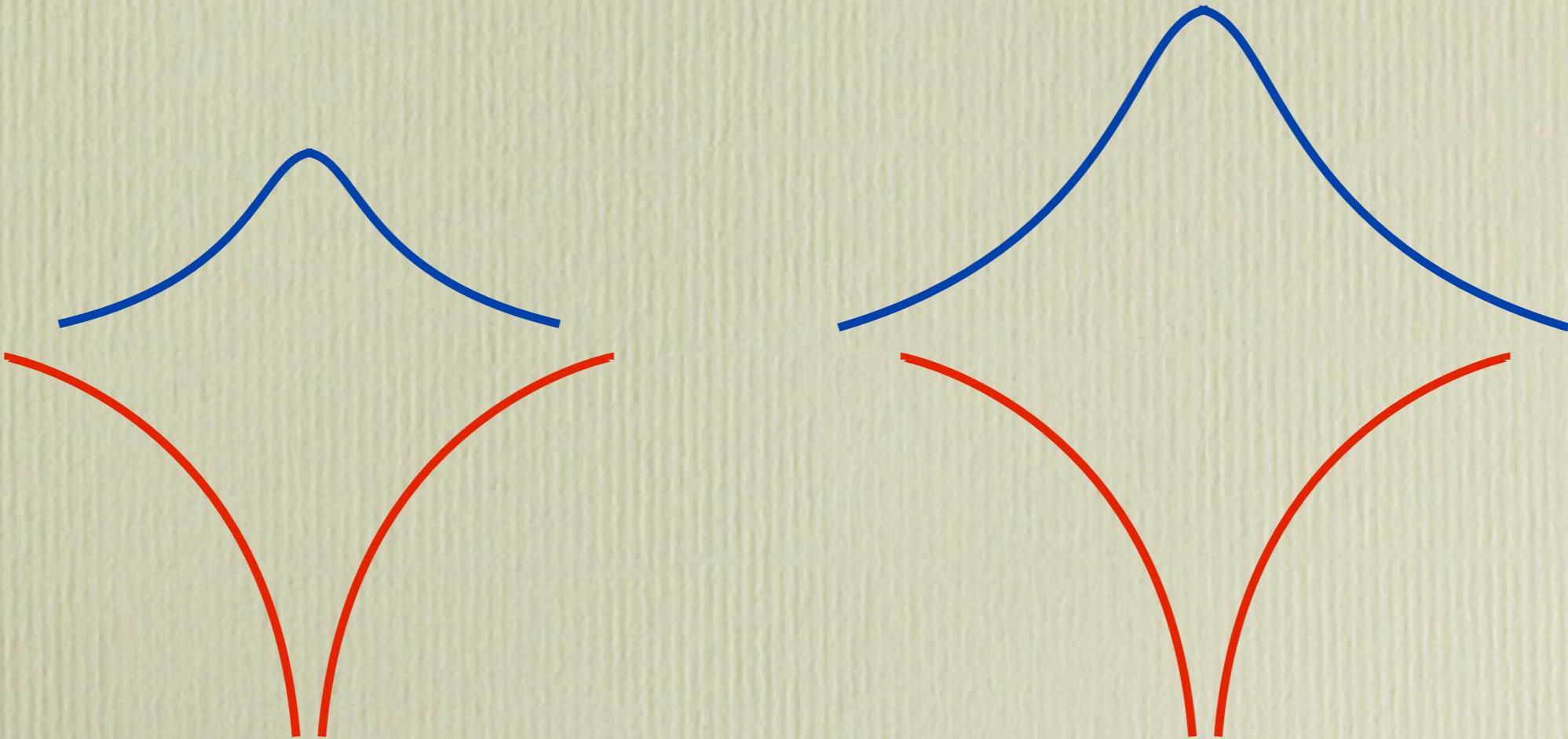
- It is included in the Induction energy:

$$E_{\text{ind}}^{(2)}[A] = \sum_{r \neq 0} \frac{|\langle \Psi_0^X | \hat{V} | \Psi_r^X \rangle|^2}{E_0^X - E_r^X}$$

- The potential \hat{V} arises from all charges (electrons and nuclei) at A.
- Let's consider the simple case where this potential arises from a single atom.

CT

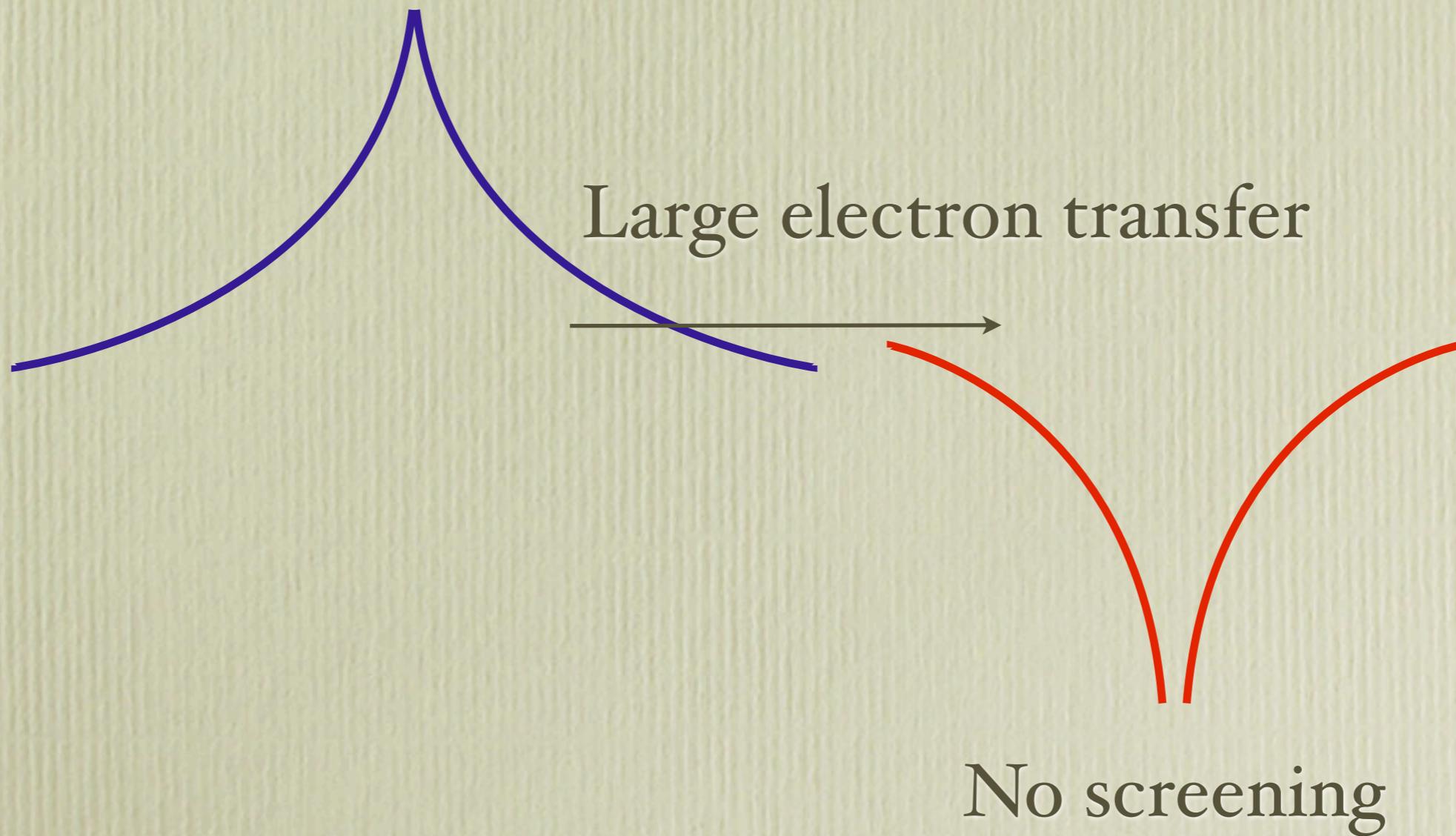
$$V(r) = -\frac{Z}{|r - R|} + \int \frac{\rho(r')}{|r - r'|} dr'$$



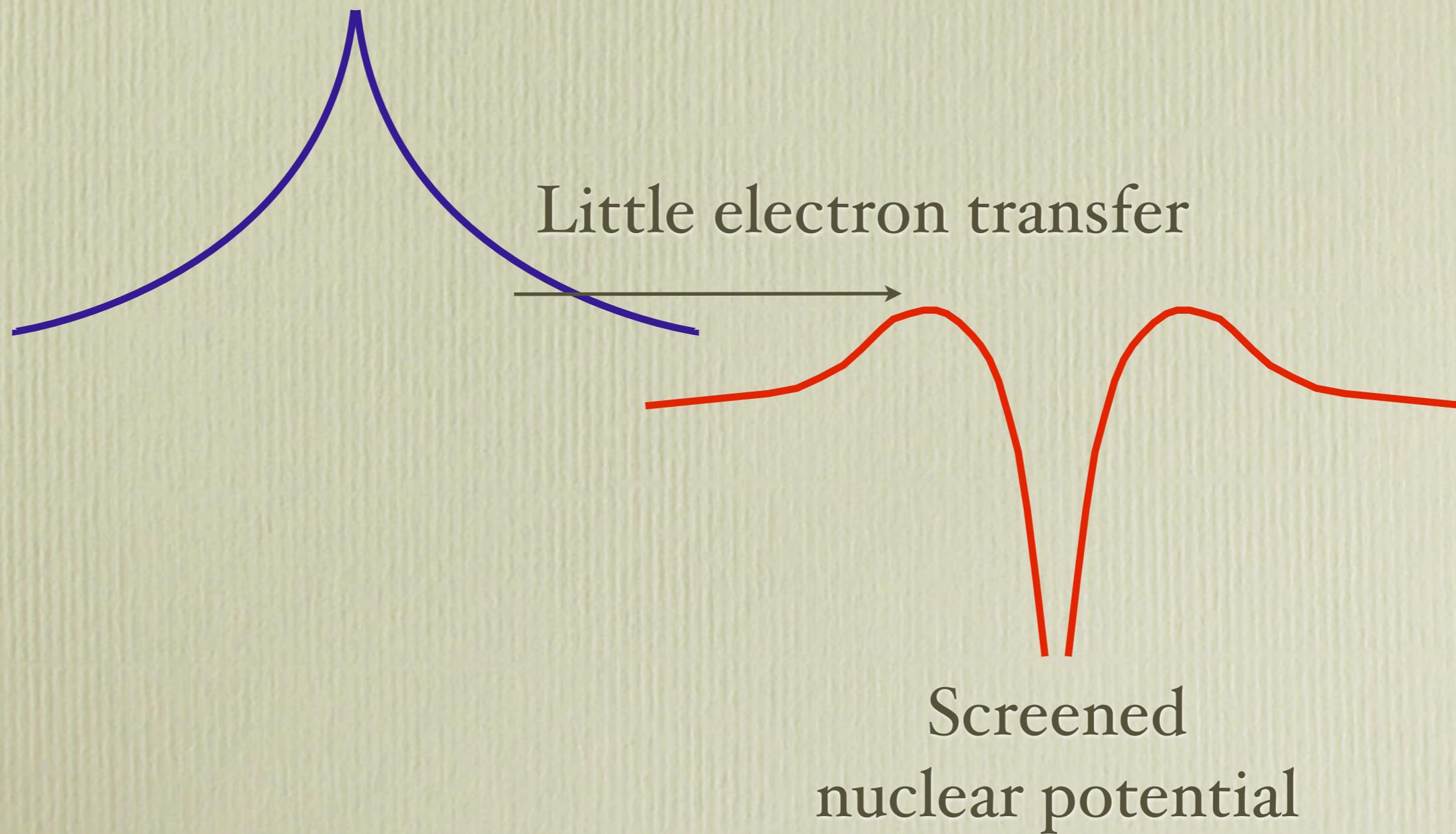
Electron deficient
Little screening

Electron rich
Strong screening

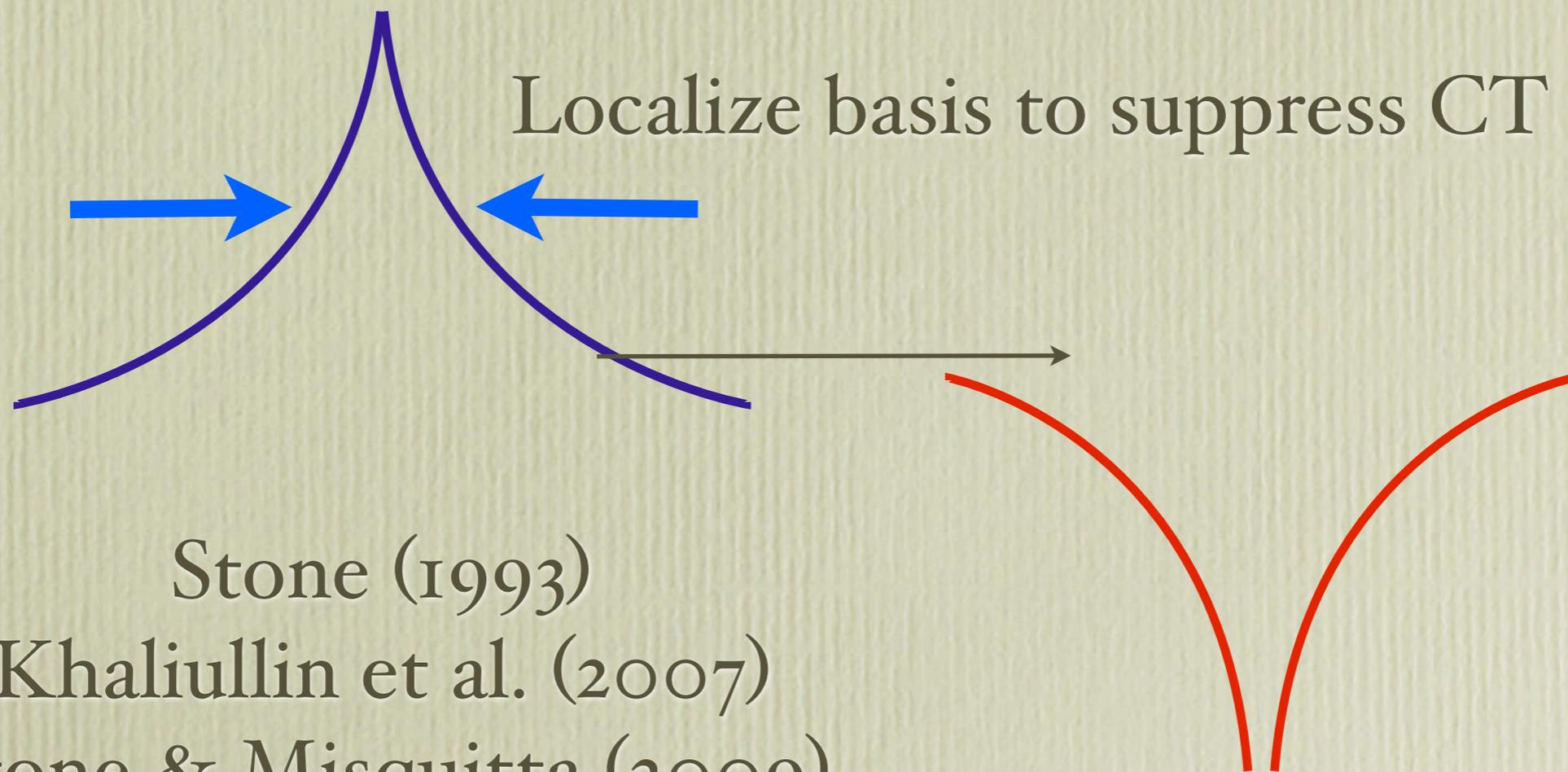
CT



CT



Suppression of CT



Stone (1993)

Khaliullin et al. (2007)

Stone & Misquitta (2009)

Define: $E_{\text{ind}}(\text{CT}) = E_{\text{ind}}(\text{DC}) - E_{\text{ind}}(\text{MC})$

CT : Stone-Misquitta

$$E_{\text{ind}}(\text{CT}) = E_{\text{ind}}(\text{DC}) - E_{\text{ind}}(\text{MC})$$

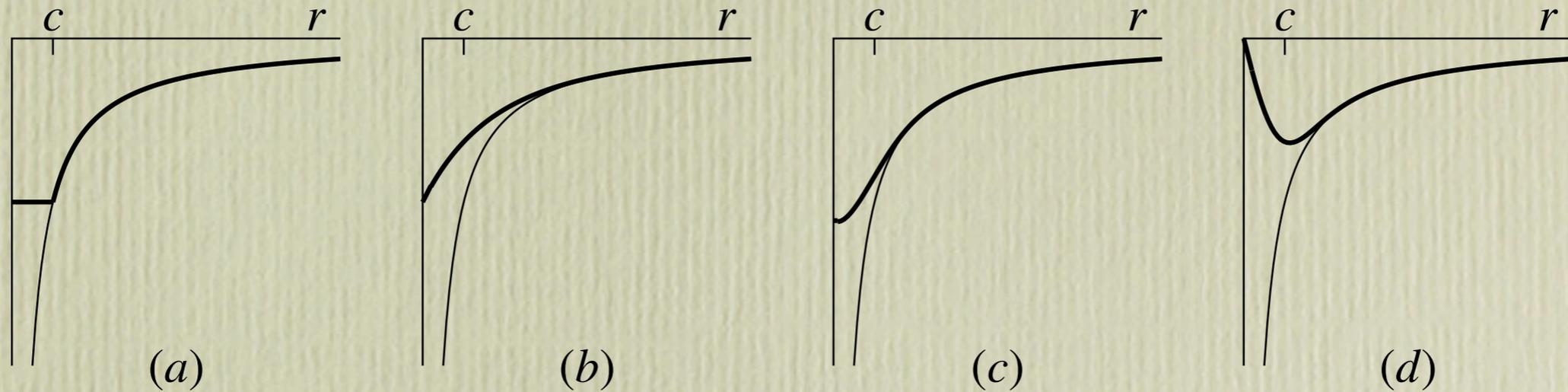
- Works, but not satisfactory as results are basis-dependent.
- Water dimer in H-bonded configuration.
Energies in kJ/mol

	aDZ	aTZ	aQZ
CT(2) S-M (2009)	-2.20	-1.42	-1.21

Khaliullin et al.: -3.5 kJ/mol

CT via Regularization

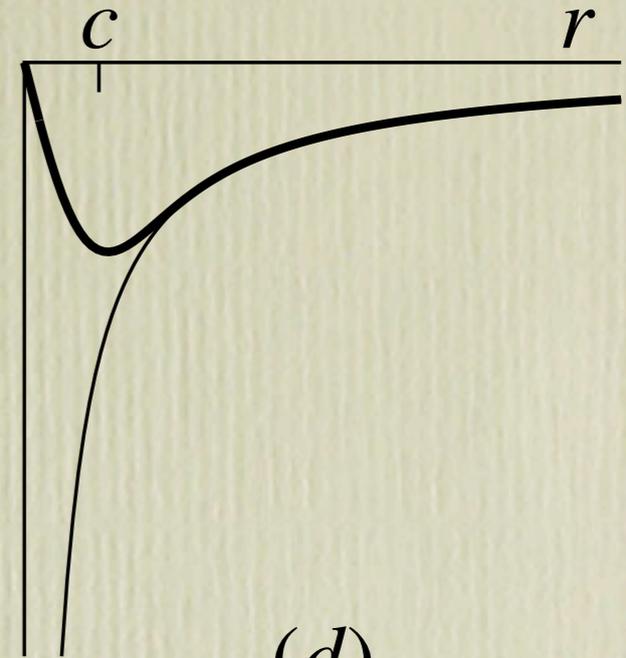
Regularization



- Proposed to cure the problem of slow convergence or divergence of perturbation theories.
- Patkowski (2001, 2004) & Adams (2002)
- R-SRS theory

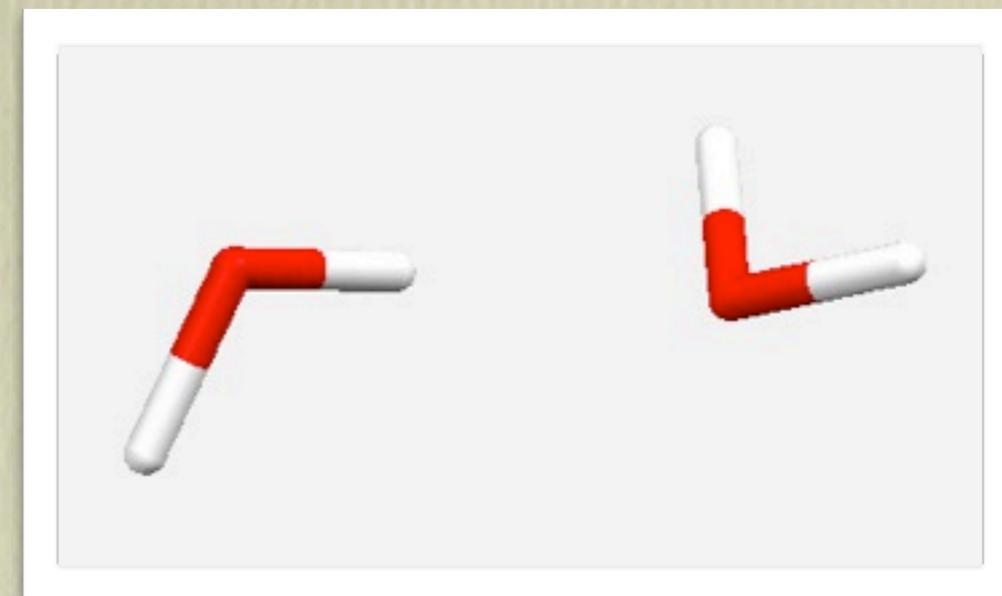
Regularized Induction

$$V_{\text{reg}}(r) = -\frac{Z}{r} (1 - e^{-\eta r^2})$$



- Patkowski et al. (in press)
- R-SRS theory: Responses calculated using regularized potential, but energy evaluated using full potential.
- Implemented in CamCASP & SAPT2008.

Basis-independent CT(2)

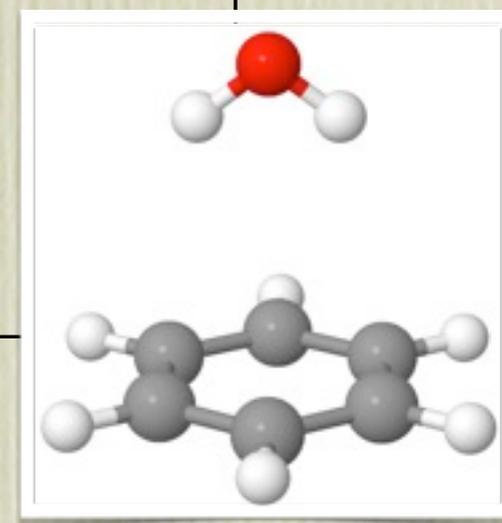
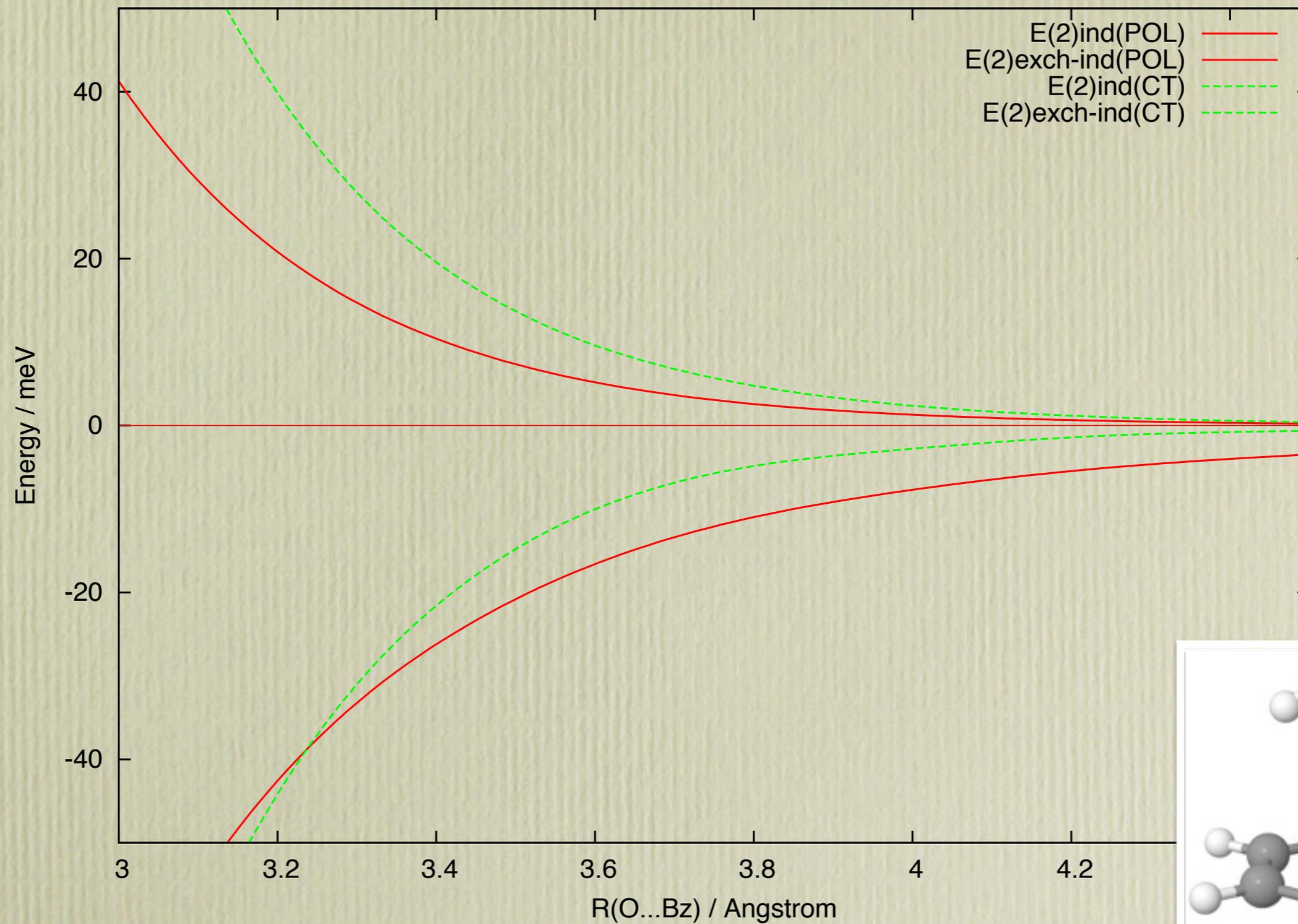


	<i>aDZ</i> <i>MC</i>	<i>aTZ</i> <i>MC</i>	<i>aQZ</i> <i>MC</i>	<i>aDZ</i> <i>MC+</i>	<i>aTZ</i> <i>MC+</i>	<i>aQZ</i> <i>MC+</i>
CT(2) S-M (2009)	-2.20	-1.42	-1.21	-	-	-
CT(2) Reg	-1.95	-1.31	-1.20	-0.95	-0.96	-0.96

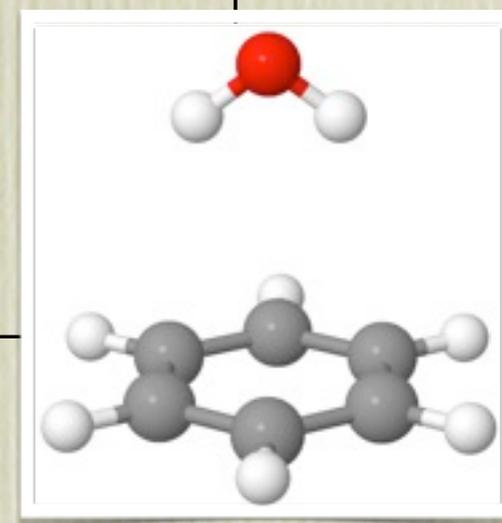
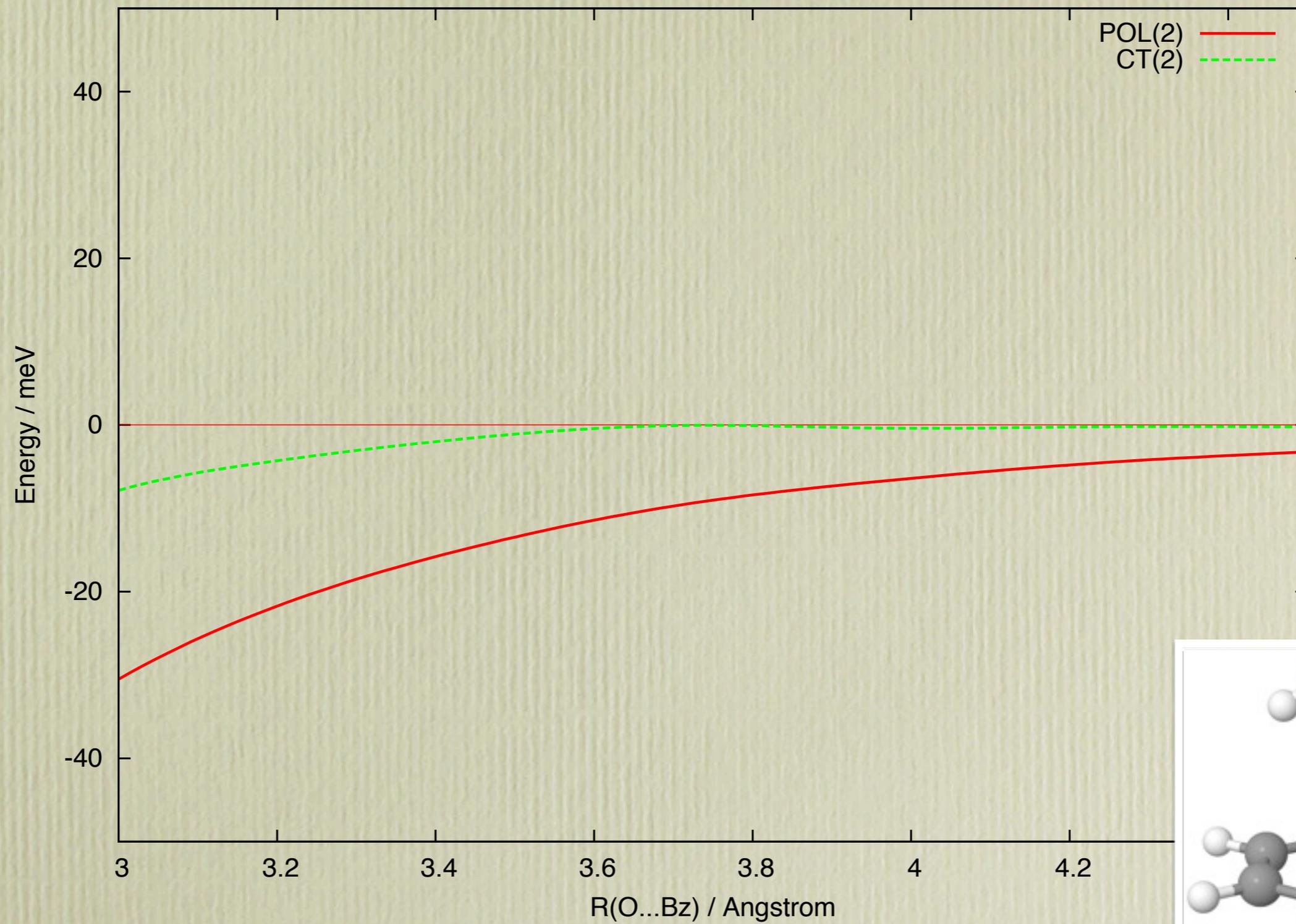
Khaliullin et al.: -3.5 kJ/mol

$\Delta H_F = -2.55$ kJ/mol

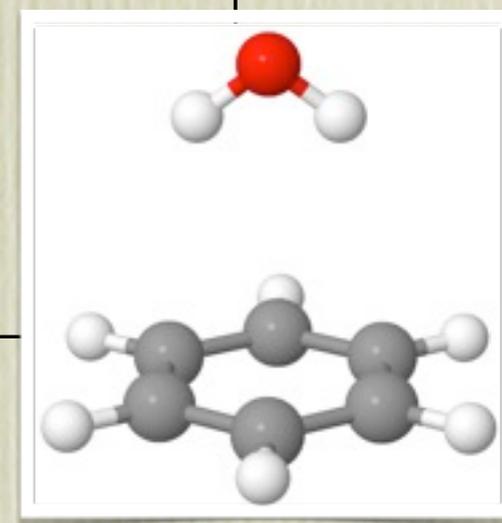
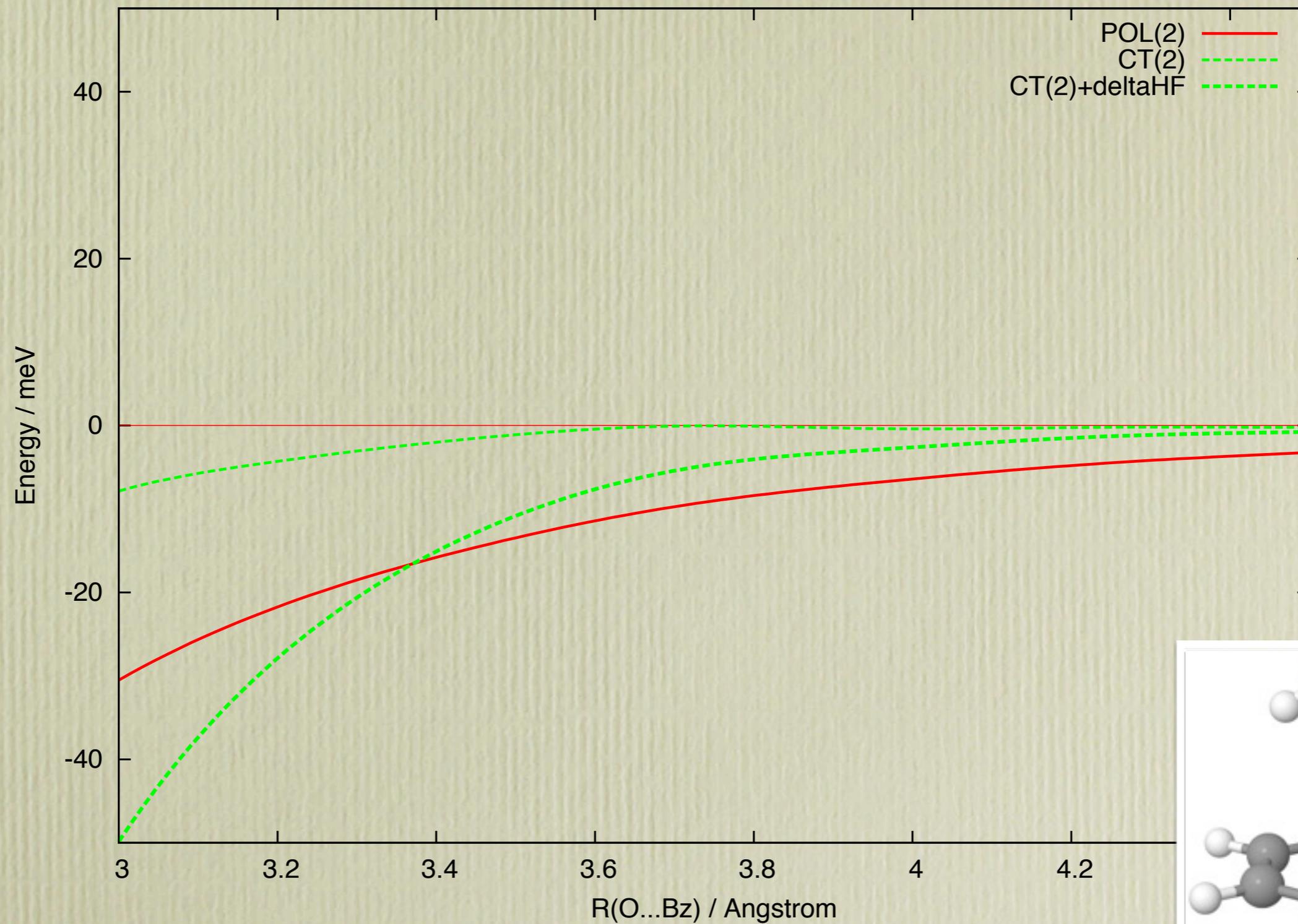
water...benzene

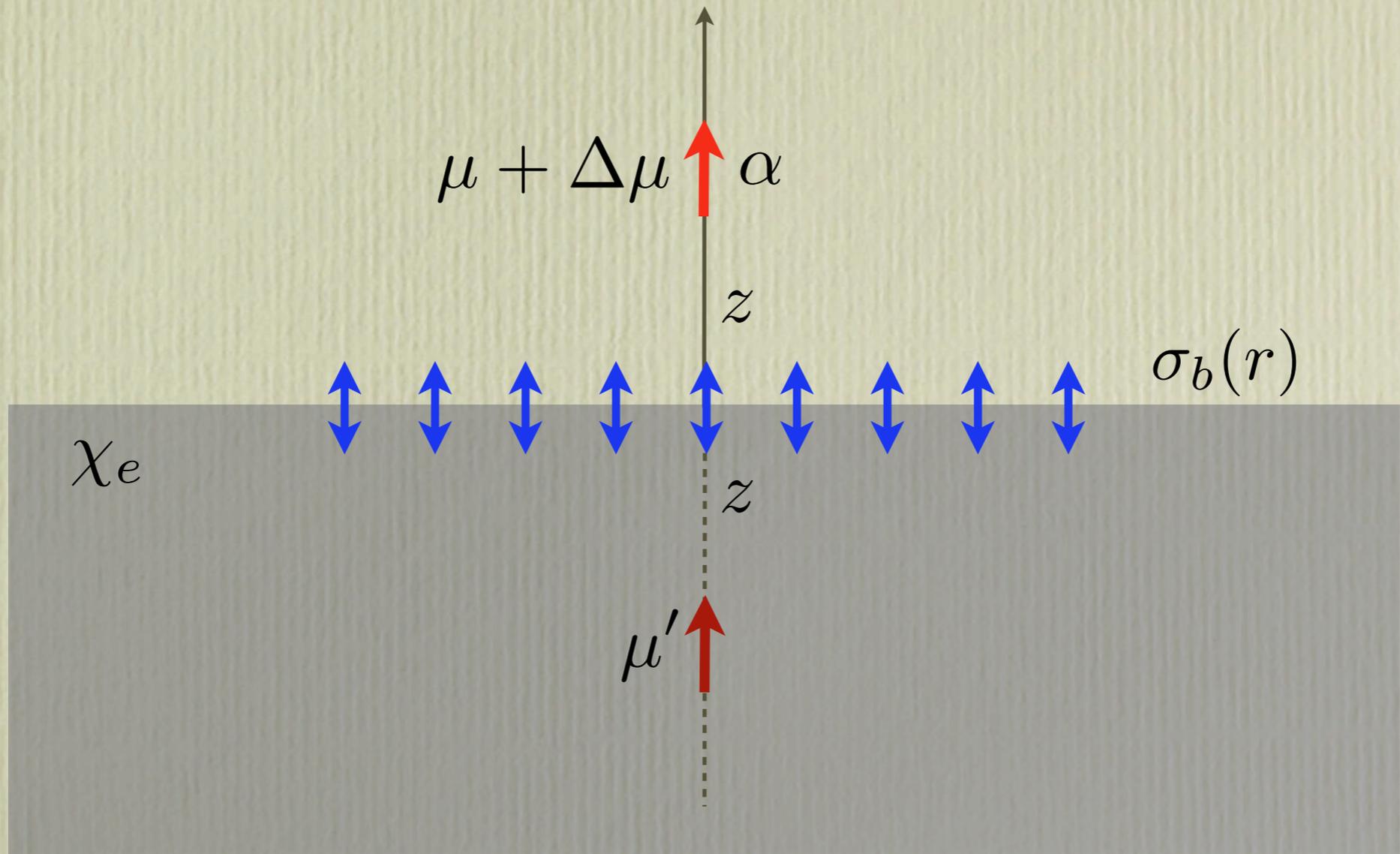


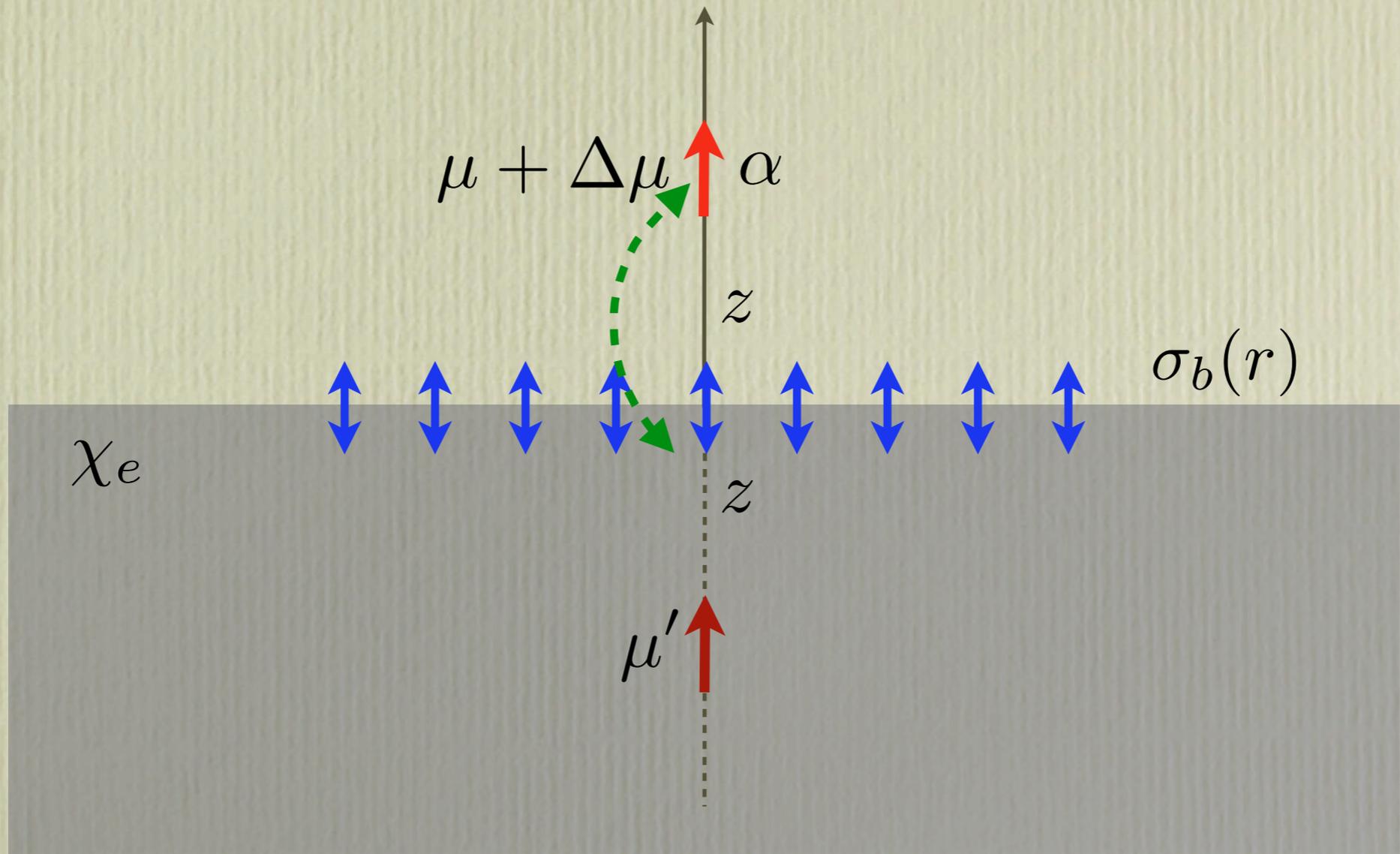
water...benzene

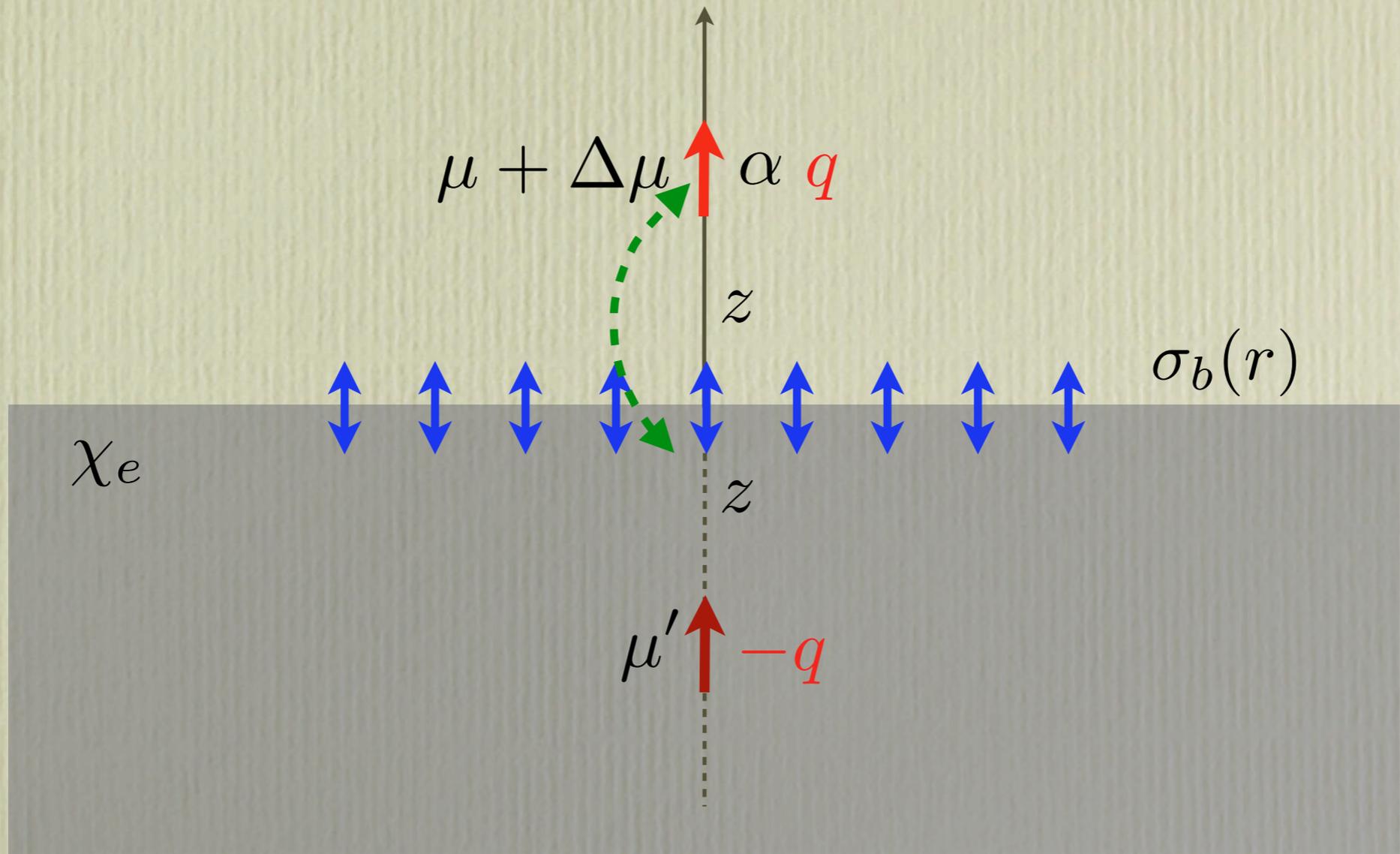


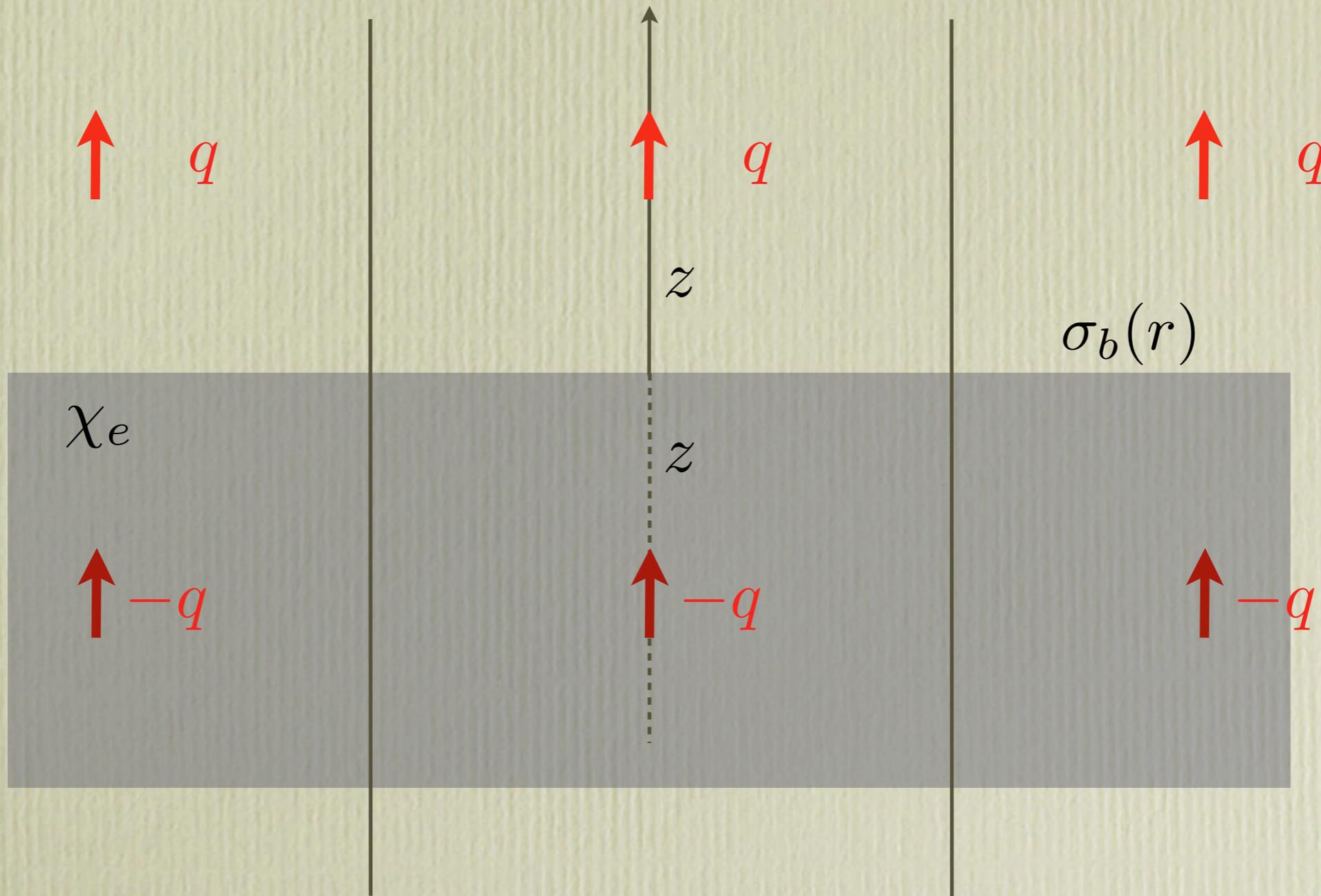
water...benzene











Charge transfer

- How do we partition the charge density to get at the actual charge transferred?
- Distribution methods like Stone's DMA result in an erratic charge allocation.
- We expect an exponential behaviour of the charge transfer as this is a tunnelling phenomenon.

Iterative stockholder approach (ISA)

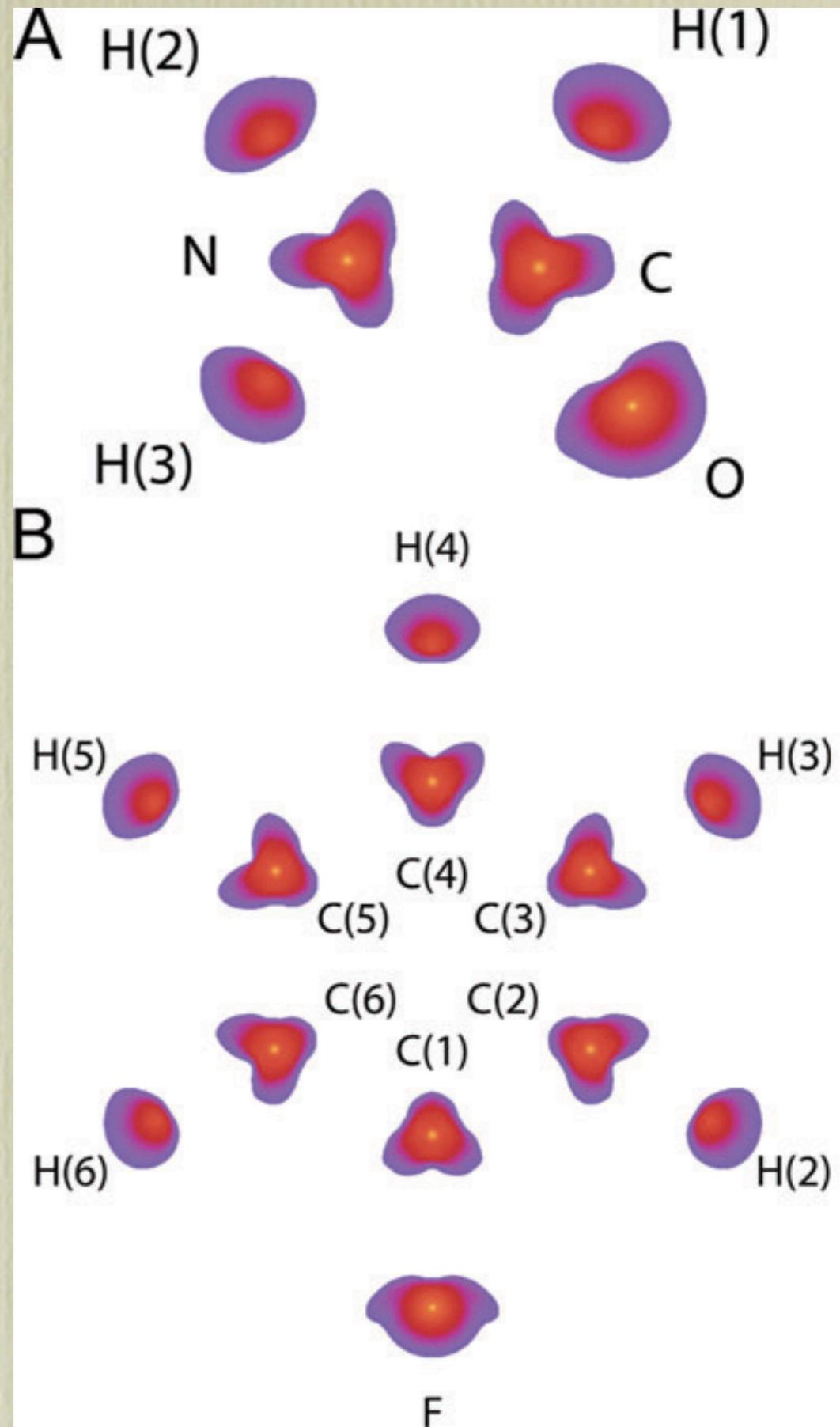
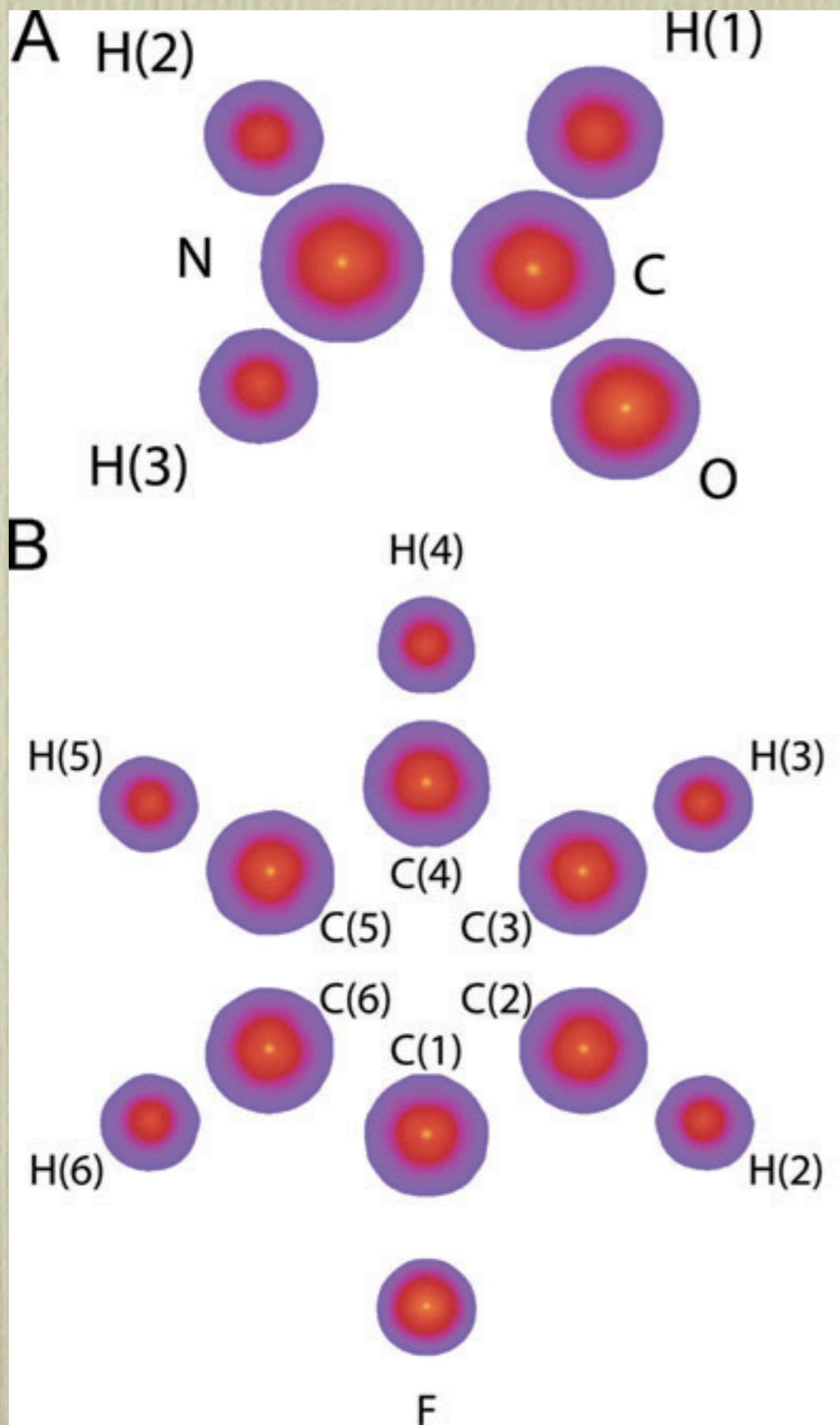
- T. C. Lillestolen & R. Wheatley, ChemComm 2008
- Given a molecular density, define atomic component densities:

$$\rho_a(r) = \rho(r) \frac{w_a(r)}{\sum_b w_b(r)}$$

- Where the shape-functions are defined as:

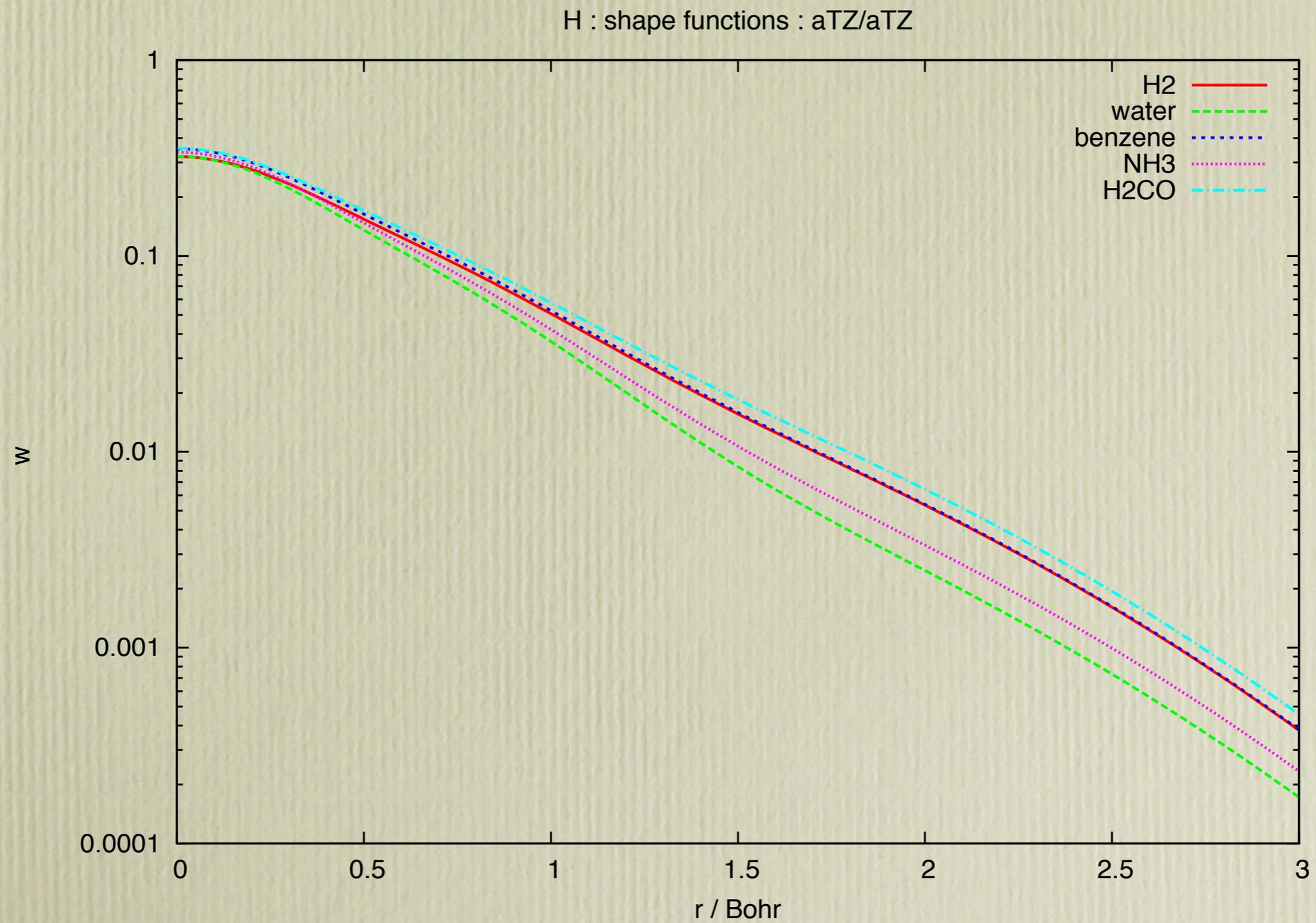
$$w_a(r) = \langle \rho_a(r) \rangle_{\text{sph}}$$

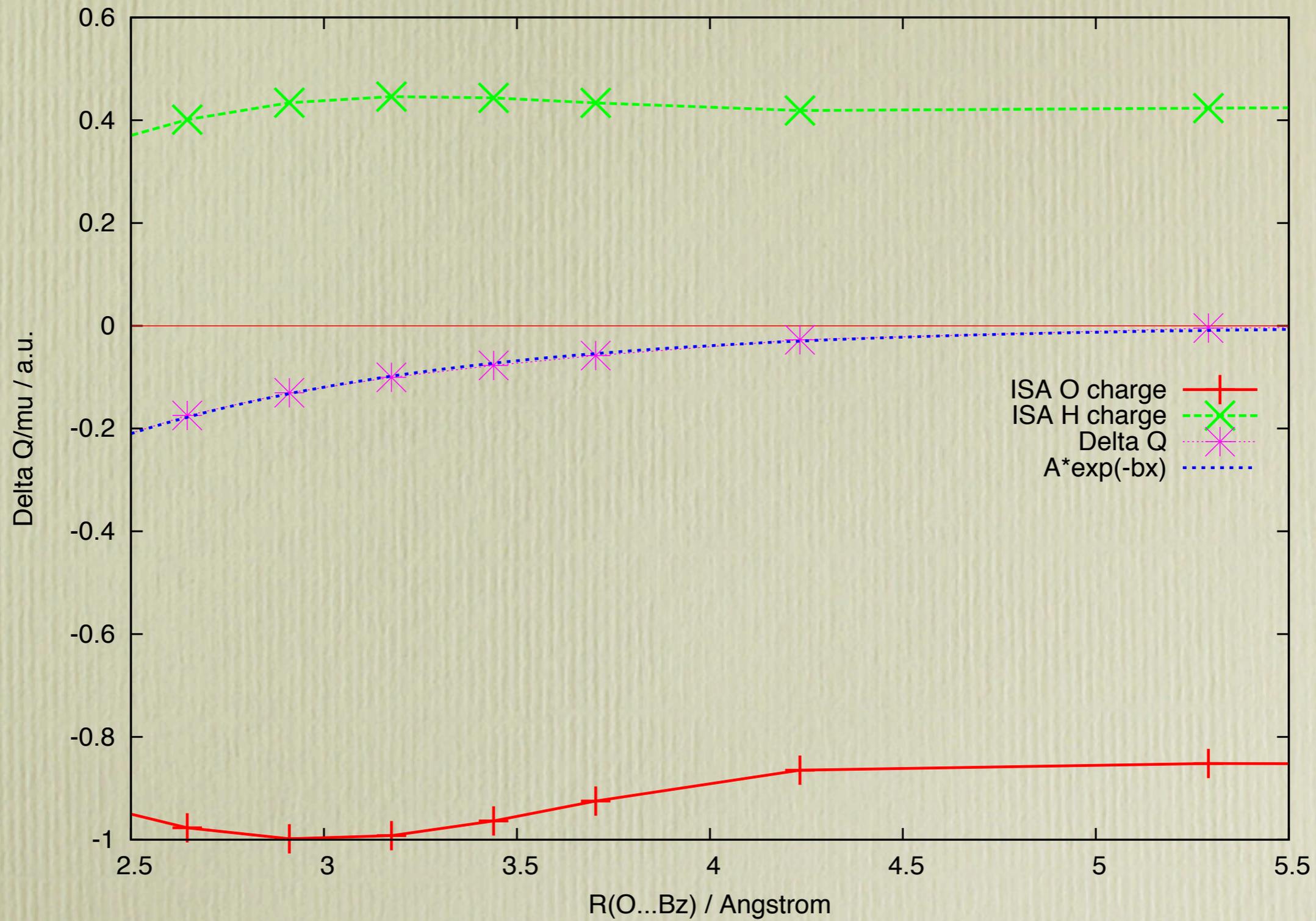
- Iterate to convergence.

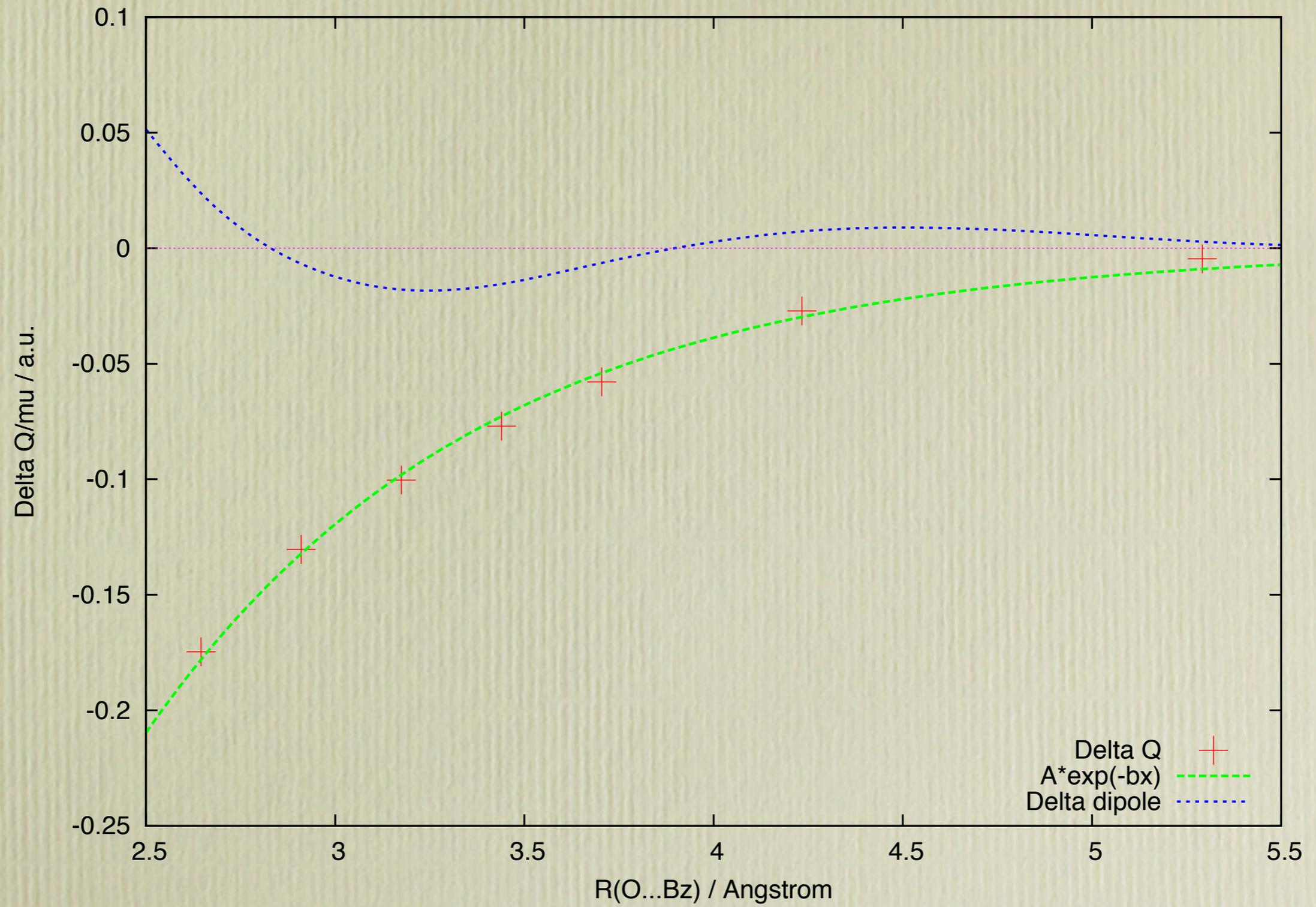


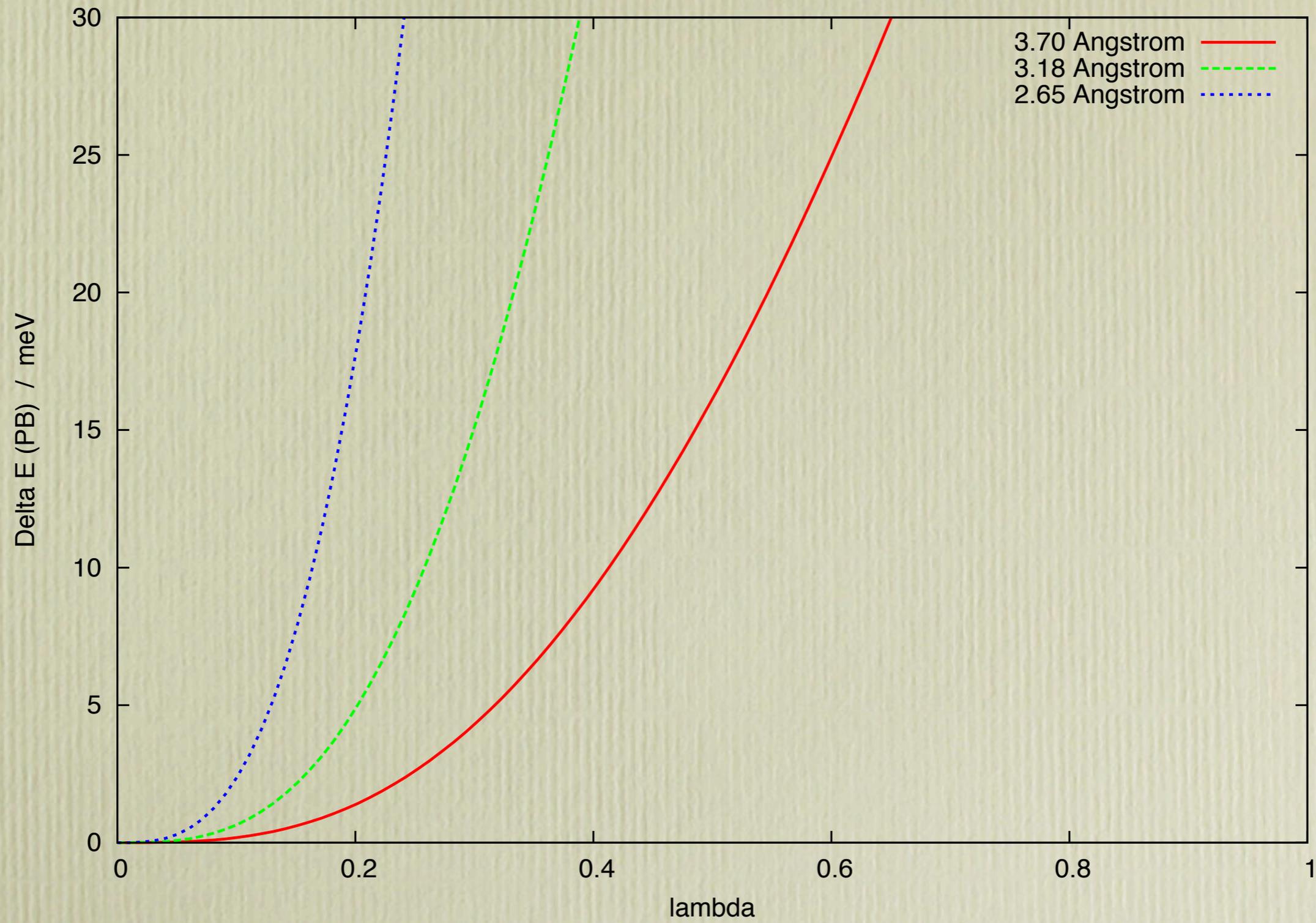
T. C. Lillestolen & R. Wheatley, ChemComm 2008

Hydrogen shape functions









Summary

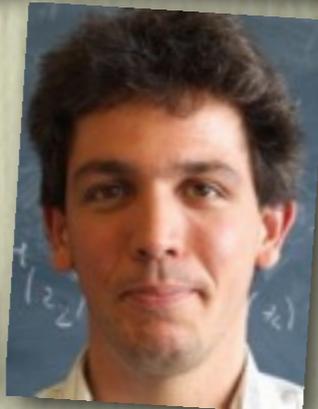
- Charge transfer appears to be the dominant cause of finite-size effects.
- Effects of the order 10 meV at $\lambda = 0.2$
- Secondary effects from induced dipoles. Unlikely to be relevant.
- Results preliminary!!! Need to be converged with size and effects included consistently.
- Potentially useful in providing analytic form for finite-size corrections.

Codes

- **CamCASP**: SAPT(DFT), WSM polarizabilities & dispersion models, GDMA2 multipoles.
- **ORIENT**: Fitting of PESs. Searches using 'Basin-Hopping'.
- <http://www-stone.ch.cam.ac.uk/>

CCMMP

- Organic semiconductors
- Functional materials
- Carbon, nanomaterials, biomaterials
- Disordered materials
- Method development



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