Towards molecules with TDDFT: basis sets

- Grid code can be used for atoms

- For efficient calculation of molecules most codes use basis sets (Gaussians)

- Want to use ADF code: how to include a wall?

- Adapt the STO basis set

Towards molecules....

- If all basis functions are 0 at the wall radius R and beyond, than any linear combination of them (i.e. AOs and MOs) must also be 0: we implicitly include a wall

$$\phi_{nlm}^{\mathrm{BSTO}}(r,\theta,\phi) = N f(r;R) \phi_{nlm}^{\mathrm{STO}}(r,\theta,\phi)$$

$$f(r;R) = \begin{cases} \left(1 - \frac{r}{R}\right) & r \leq R \\ 0 & r > R \end{cases}$$

$$\phi_{nlm}^{\mathrm{STO}}(r,\theta,\phi) = r^{n-1} e^{-\alpha r} Y_{lm}(\theta,\phi)$$

- A smaller wall distance R limits the number of functions necessary but it must be outside of the range of the density and/or the range of the occupied orbitals.

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$$f(r; R) = \begin{cases} \left(1 - \frac{r}{R}\right) & r \leq R \\ 0 & r > R \end{cases}$$

The first derivative is not zero in this case. Taking a numerical derivative therefore leads to problems.

All derivatives are taken analytically.
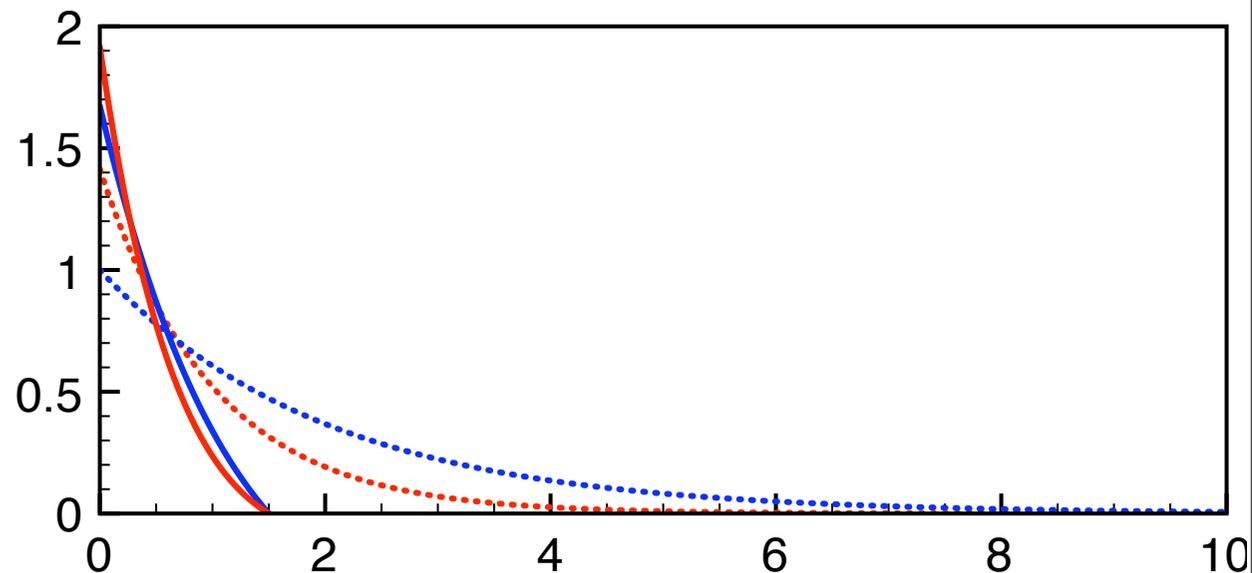
# Another intermezzo: compressed atoms

- We will see that BSTOs can be used to describe scattering functions

- But we can also use them to describe *compressed atoms*

- Compressed systems are very interesting to study, we can study the effect of pressure exerted on an atom

- For example, atom in buckyball, impurity in solid, atom in zeolite cage etc...
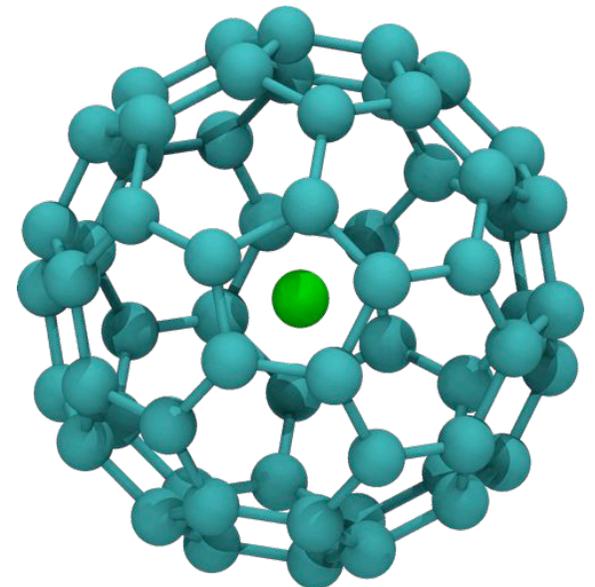
Another intermezzo: compressed atoms

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The implementation of BSTO functions in ADF allows for the calculation of properties of compressed atoms _and_ continuum functions (in a box)
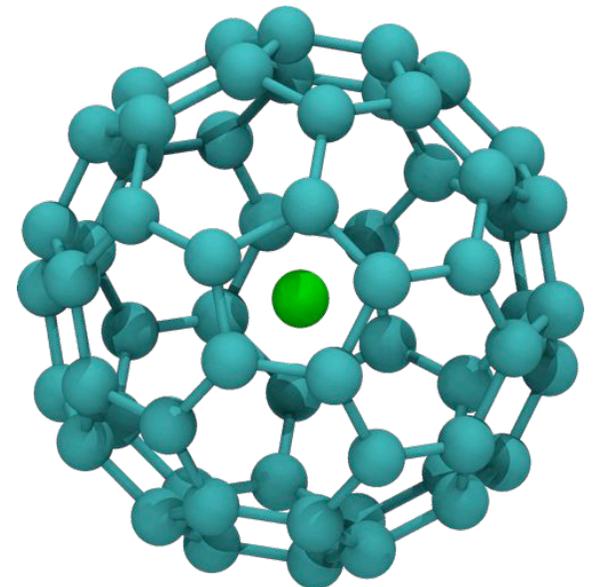
Square well in a box
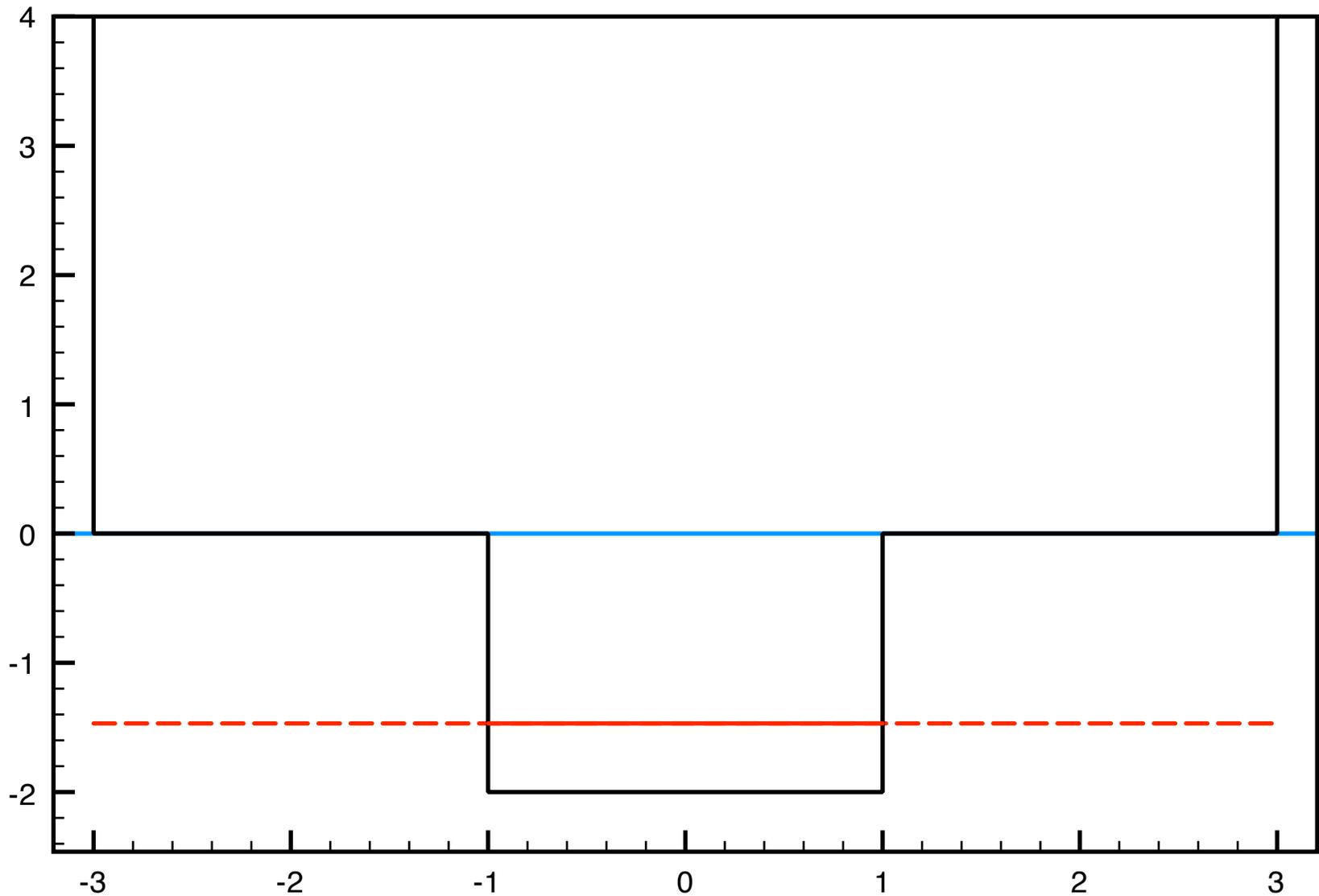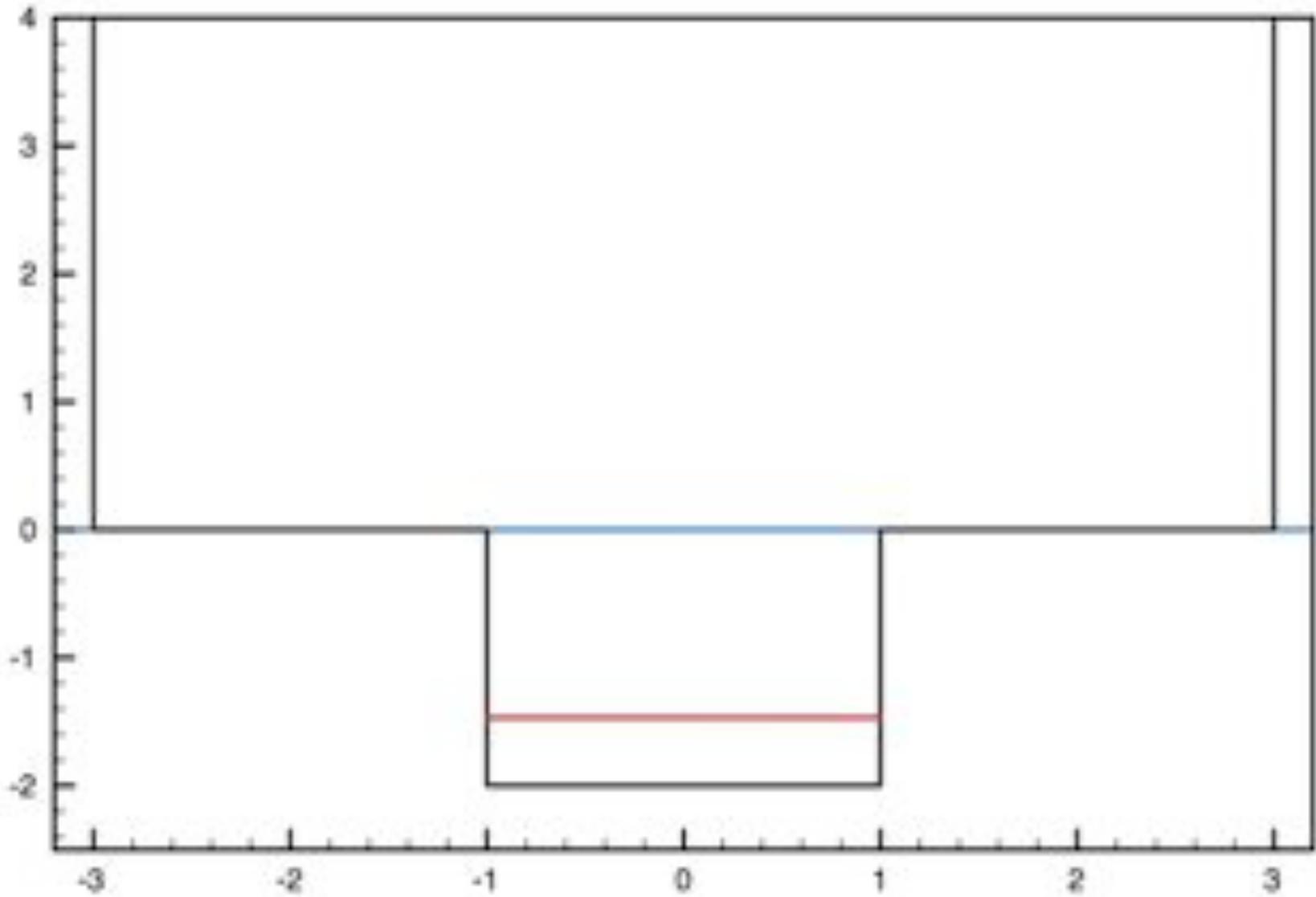
Square well in a box

Square well in a box

- The energy of the occupied level rises and passes through zero at the ionization radius

- The polarizability has an S-shaped curve, going like R^4 in the "particle in a box" region and converging from below to the free value
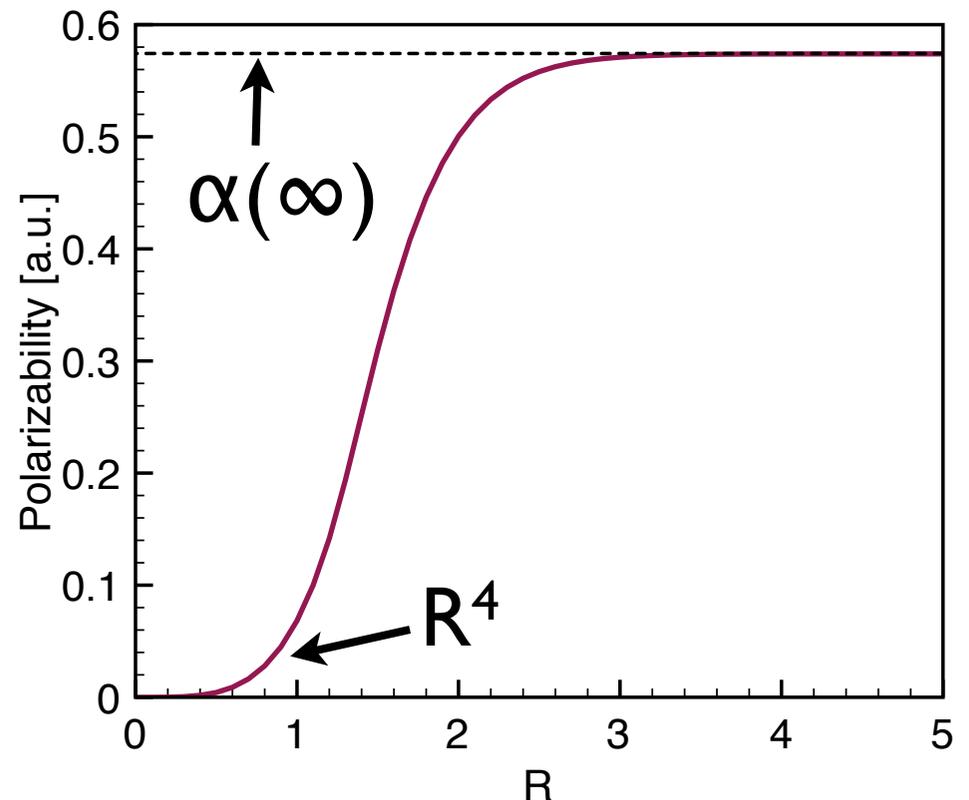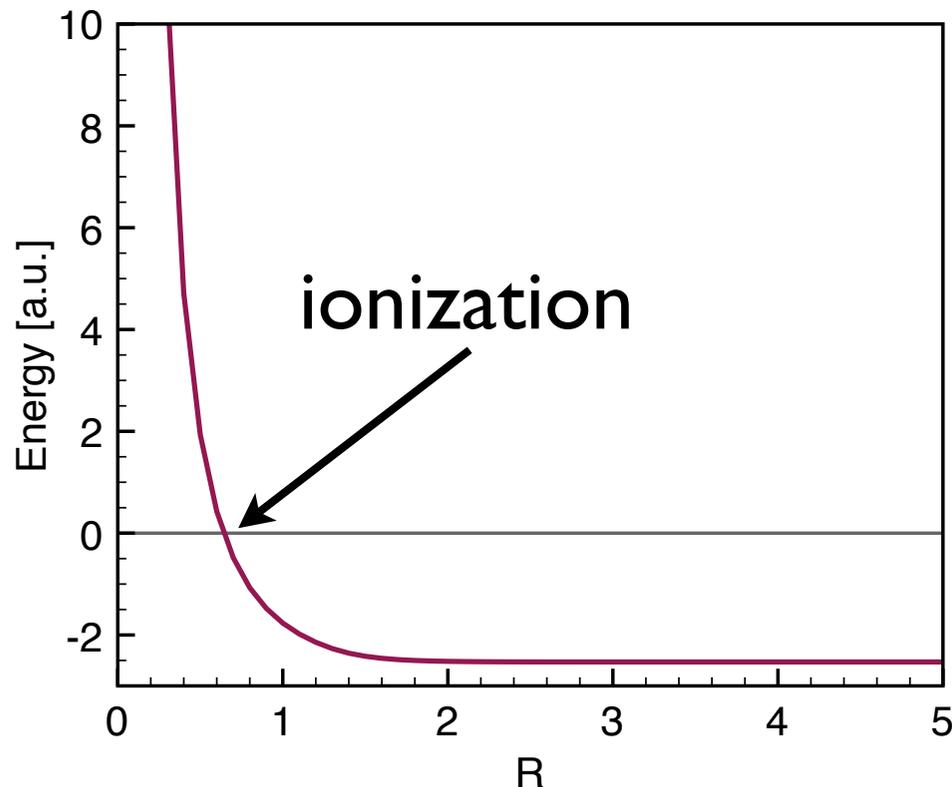
Properties of confined atoms

- HOAO orbital energy of He and Ne:

    - HF results available (PW91 for ionization radius)

    - DFT SAOP energies

- Polarizability of He and Ne:

    - only finite field HF calculations available

    - TDDFT SAOP/ALDA static polarizabilities

HOAO vs R

We see the same behavior as for the square well

Ionization radii (bohr):

	HF	PW91	SAOP
He	1.41	-	1.50
Ne	1.83	1.83	1.89
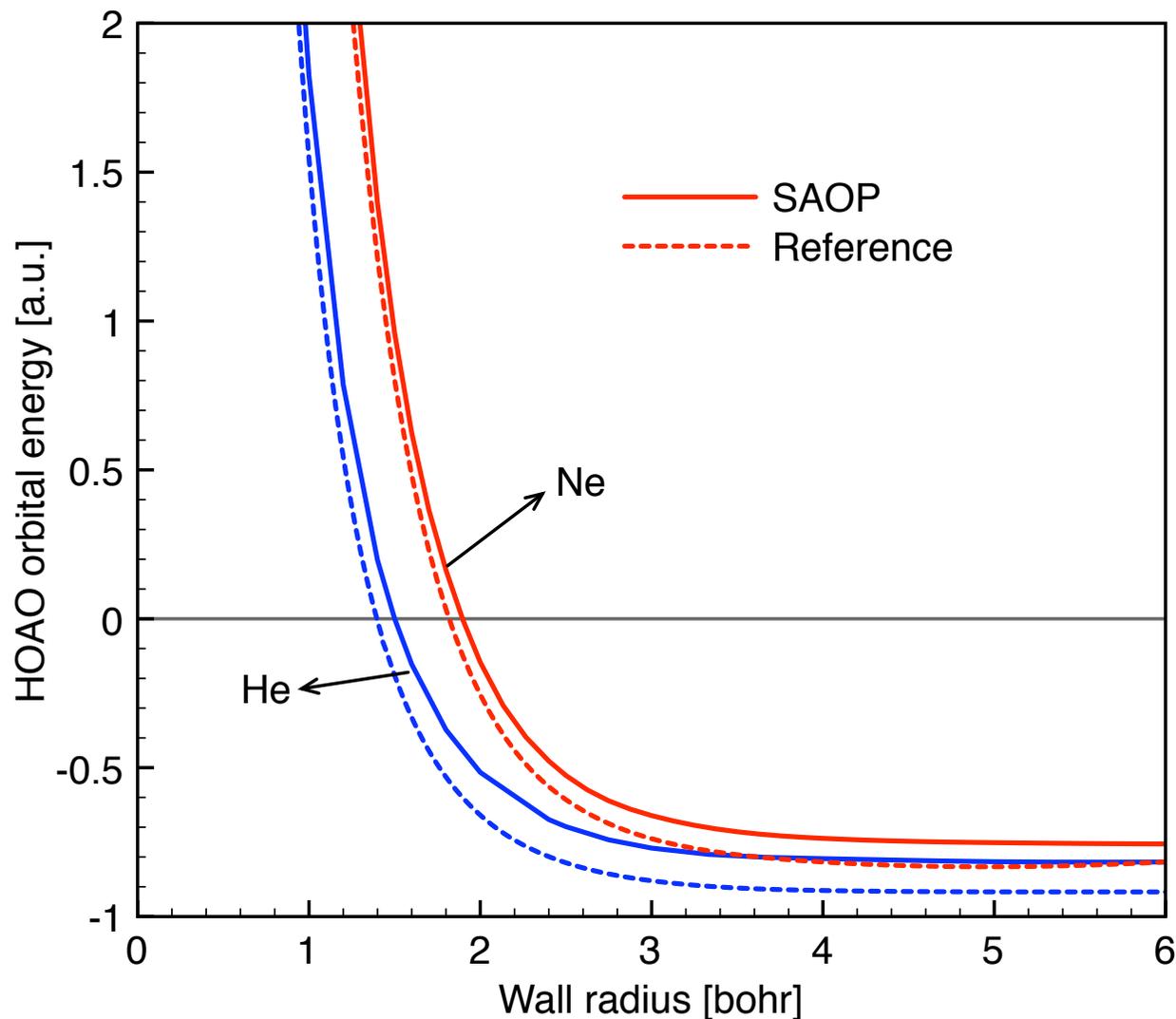
HF: Ludena, E. V. , J. Chem. Phys. **69** (1978)1770
PW91: Garza, J., Vargas, R., Aquino, N., and Sen, K., J. Chem. Sci. **117** (2005) 379

Polarizability vs R

We obtain an S-shaped curve in both cases

Similar S-shaped curves were found from HF for a range of atoms

Slow convergence of Ne polarizability to the free atom value

P. Chattaraj and U. Sarkar, Chem. Phys. Lett. 372, 805 (2003).


SAOP/ALDA

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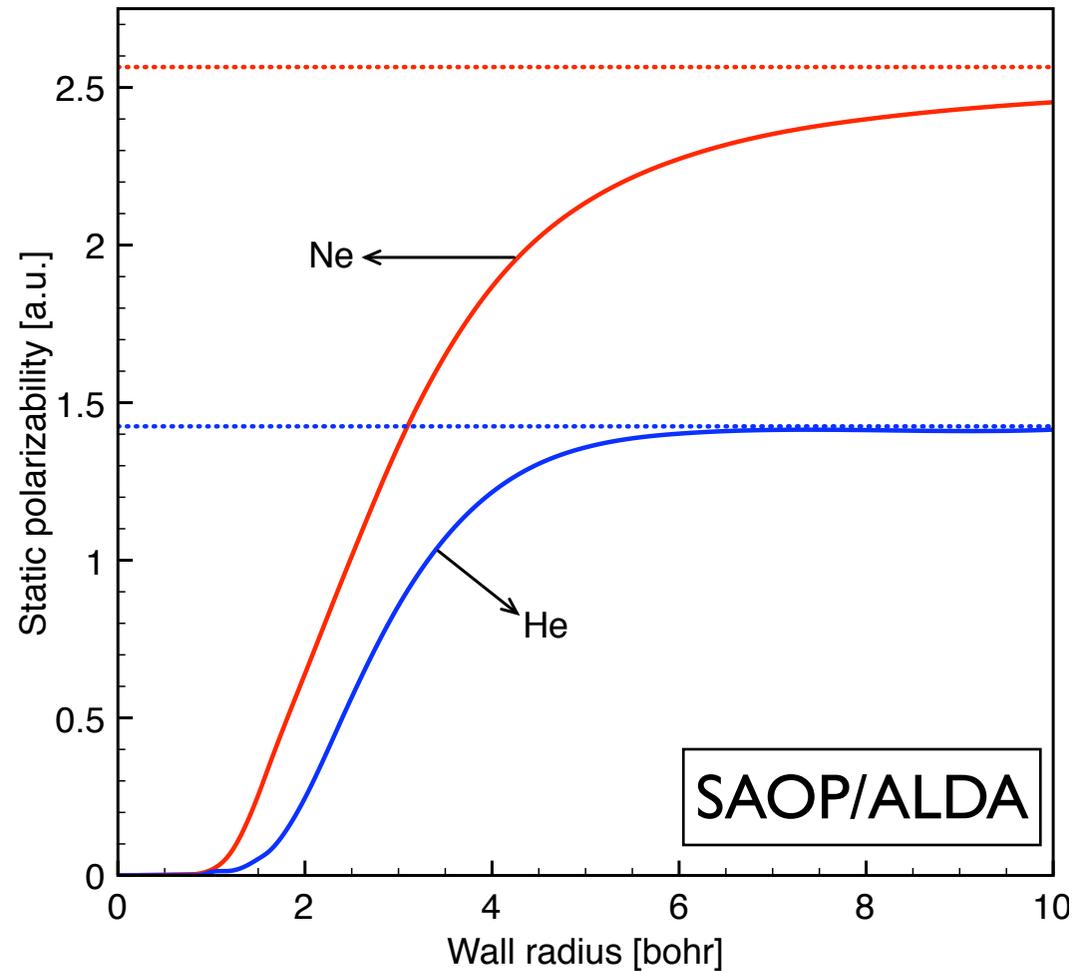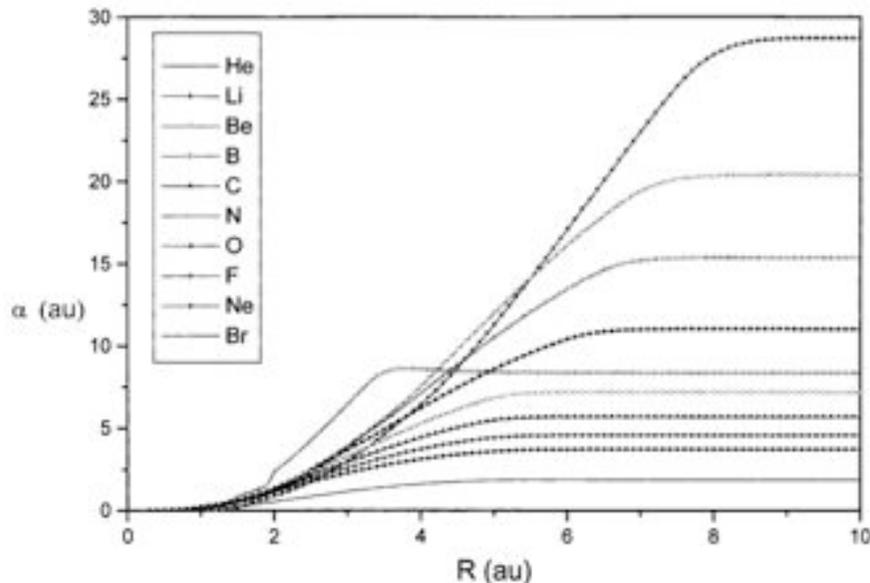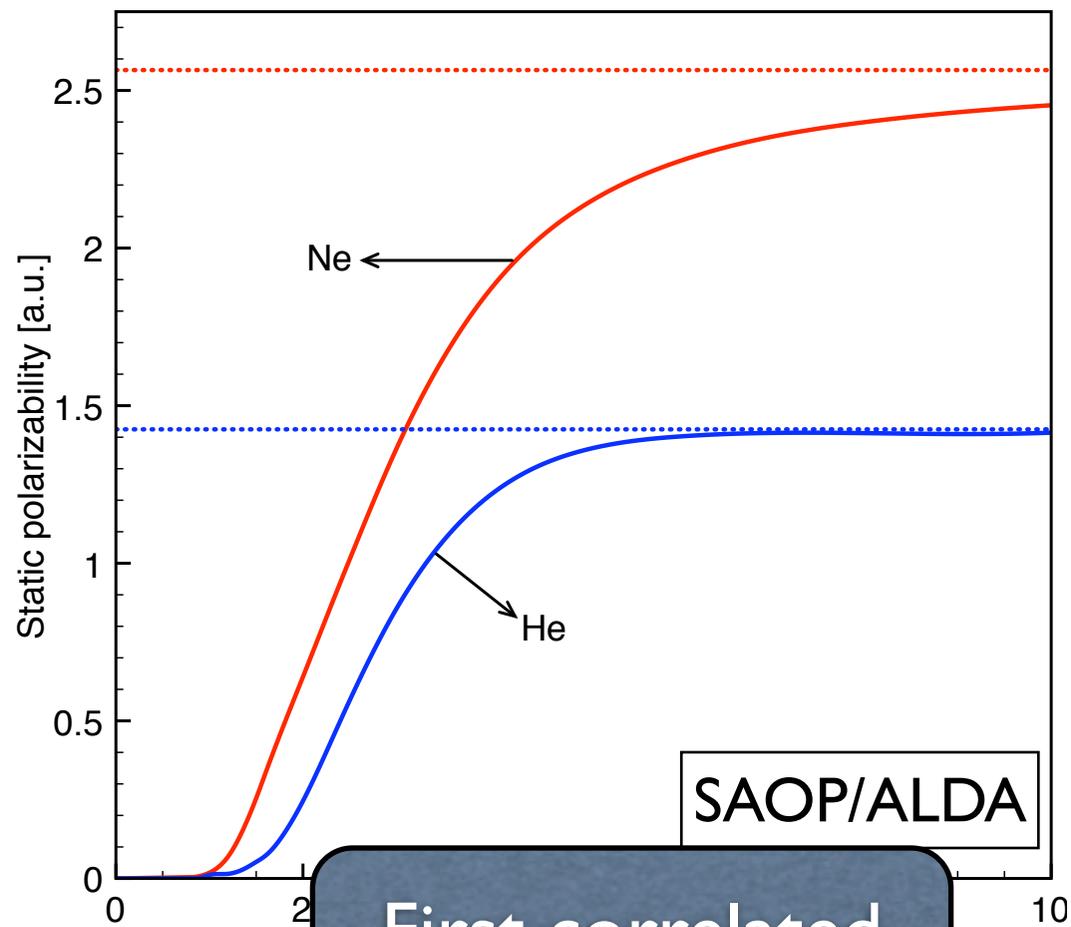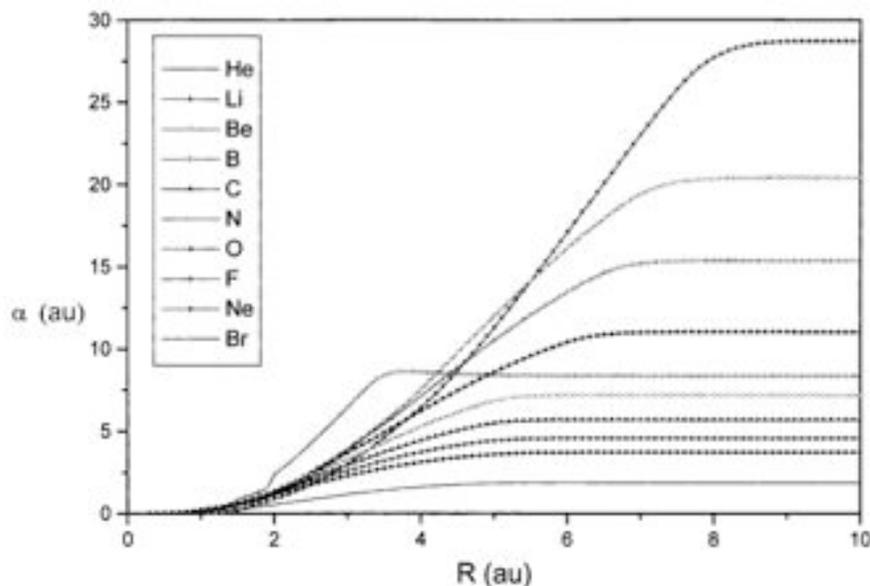
First correlated results for more than 2 electrons

Continuum functions from BSTOs

- Our basis set needs to describe the oscillatory behavior of the continuum states

- B-spline basis sets are suitable

- Our BSTO basis set, if chosen properly, turns out to be suitable as well
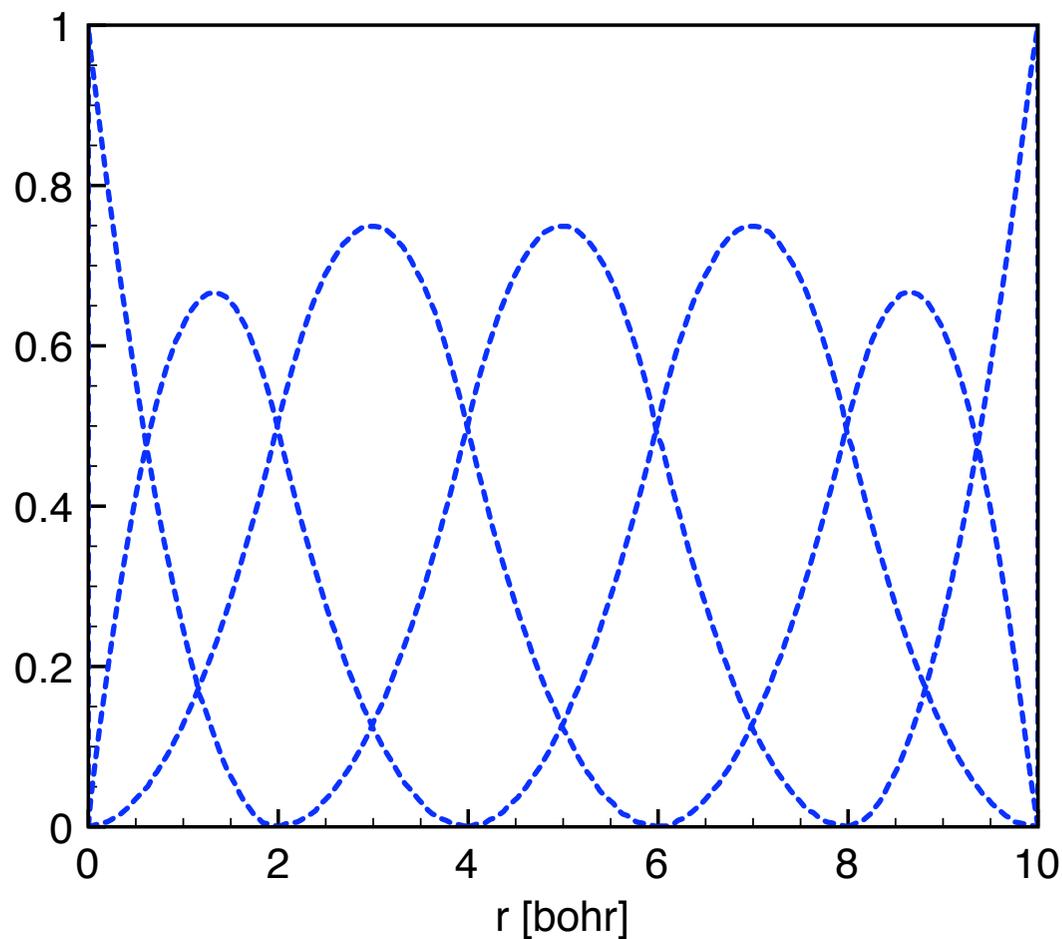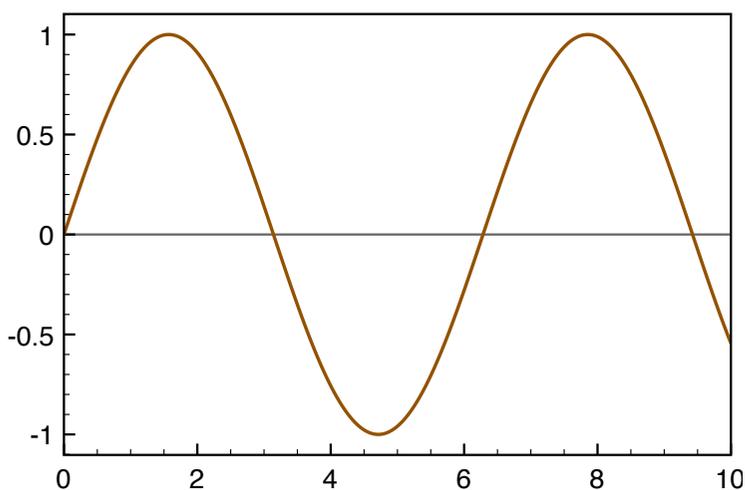
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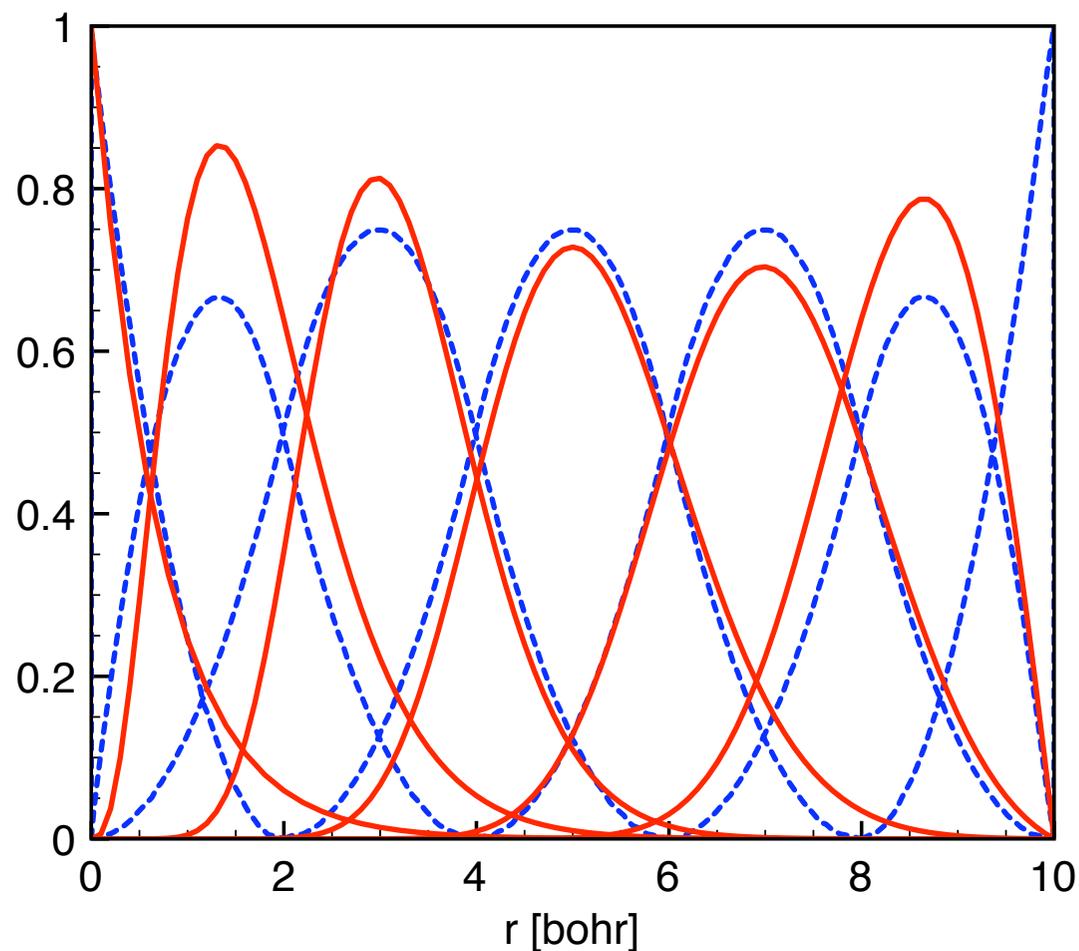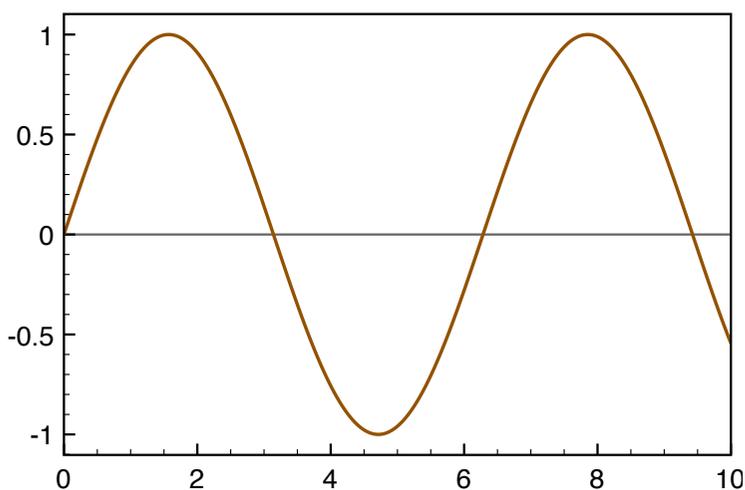
Parameters for the BSTO set

- A smaller wall distance R limits the number of functions necessary but it must be outside of the range of the density and/or the range of the occupied orbitals.

$$F^{\mathrm{BSTO}} = N \left(1 - \frac{r}{R} \right) r^{n-1} e^{-\alpha r}$$

- At a BSTO function maximum (n > 1) we have the relation

$$\alpha = \frac{r + n(r - R)}{r(r - R)}$$

- The maxima are distributed evenly and n determines the "width" of the functions (n is chosen, alpha determined by n and R)
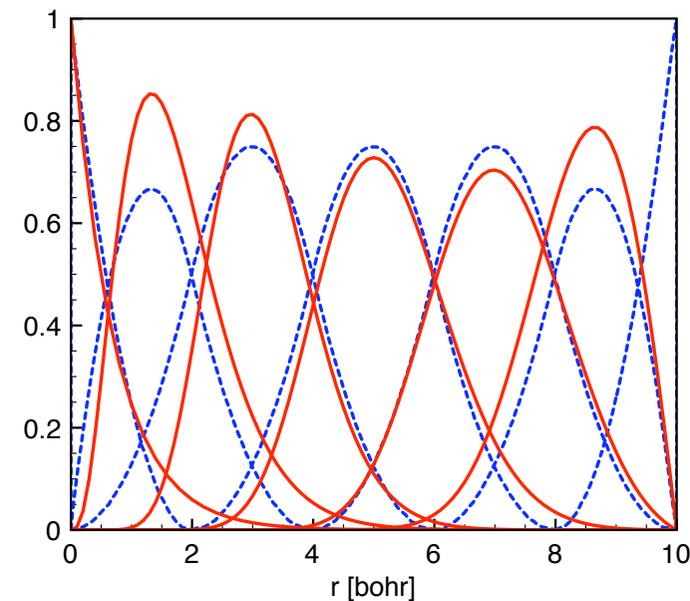
e-H scattering

- BSTO results (markers) are on top of the grid code results

- Three wall distances already determine most of the curve
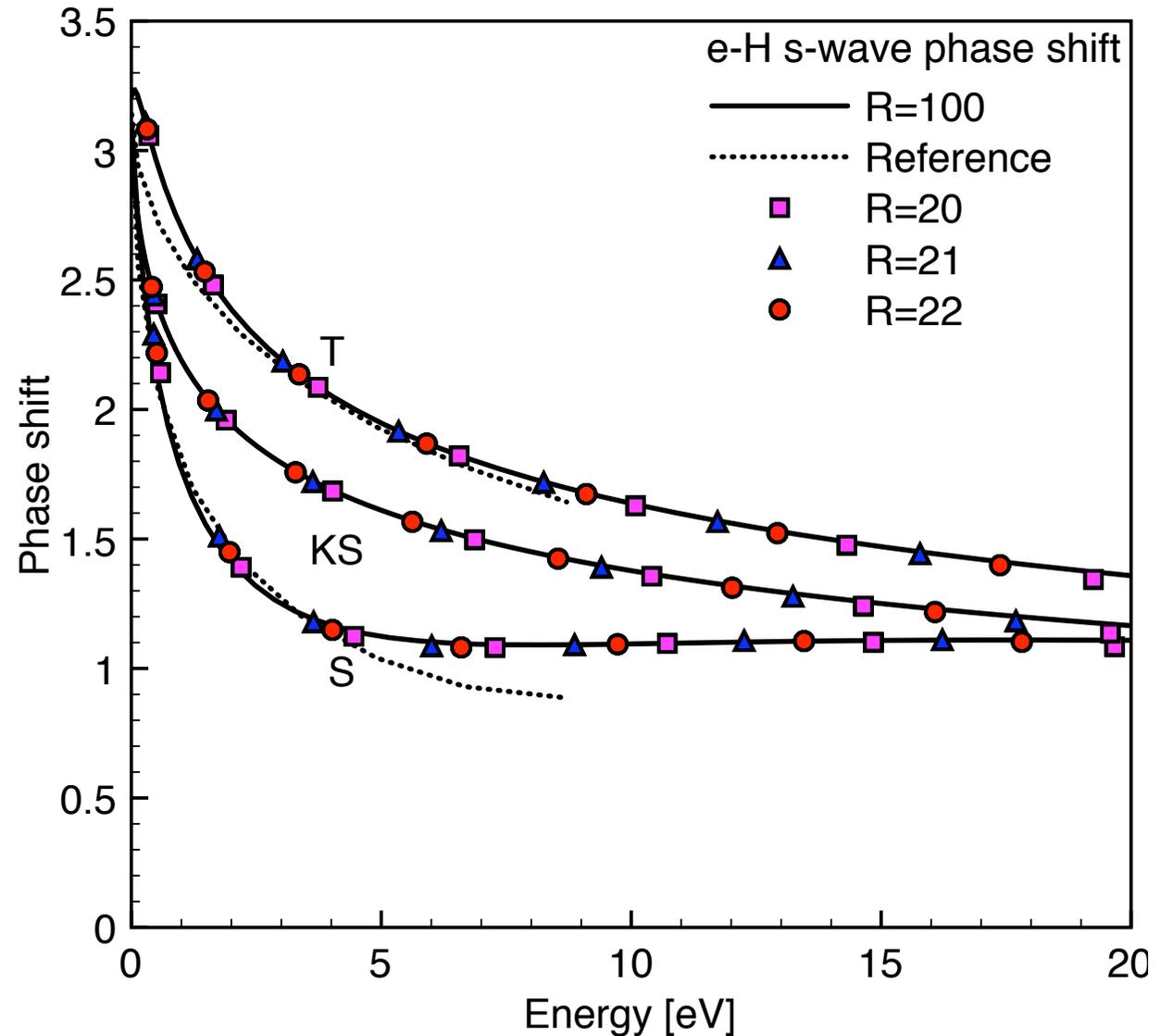
e-He+ scattering

- BSTO results (markers) are on top of the grid code results

- Three wall distances already determine most of the curves

- s and p curves are both well described
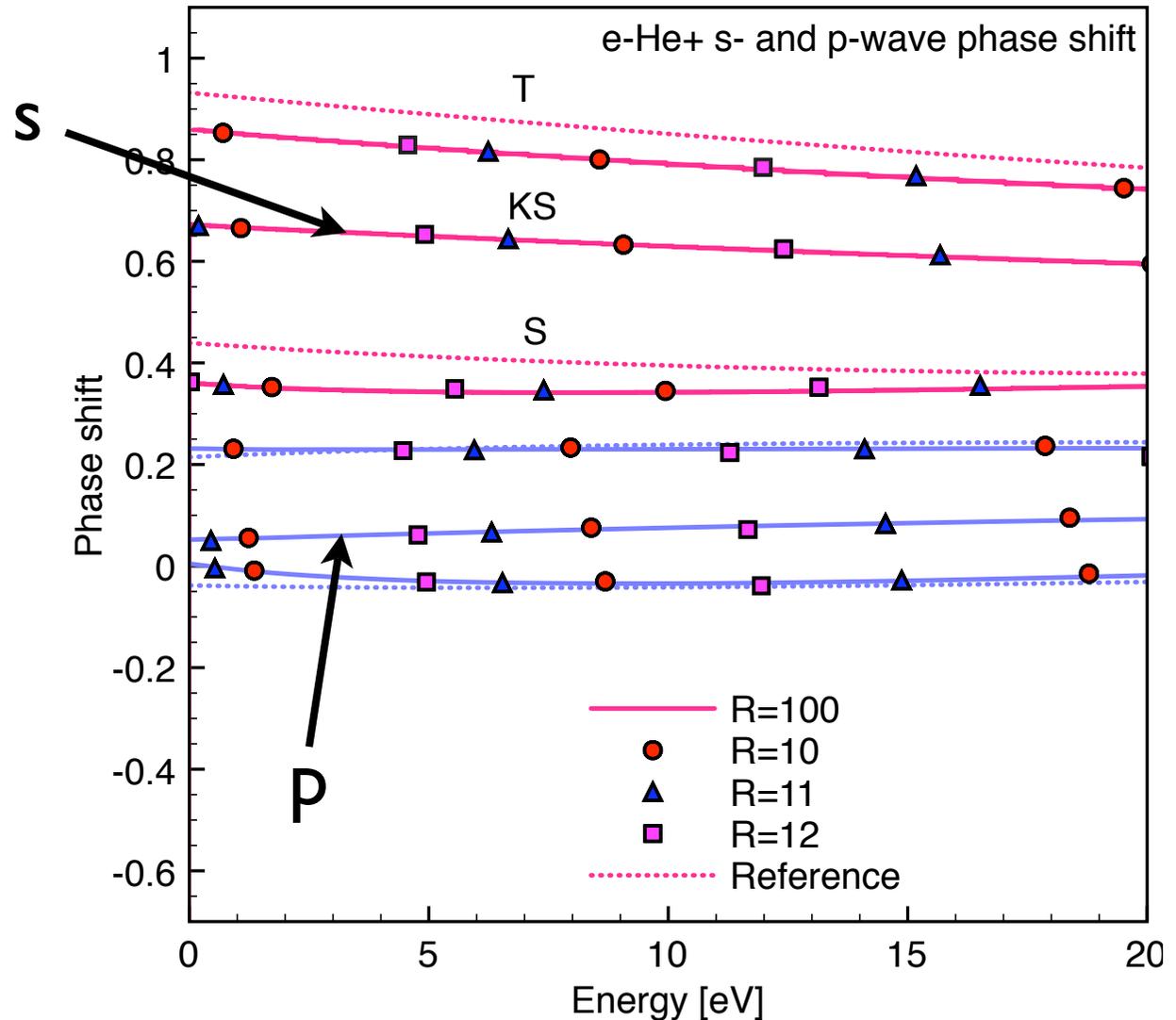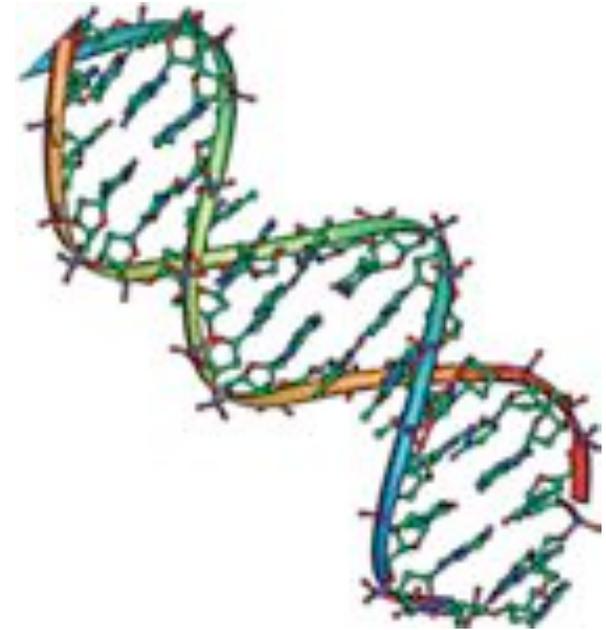
MOLECULES

Molecules: non-spherical systems

- The fact that molecules are non-spherical complicates matters

- The results are dependent on the scattering angle and the molecule might break up and fragments can fly away in any direction
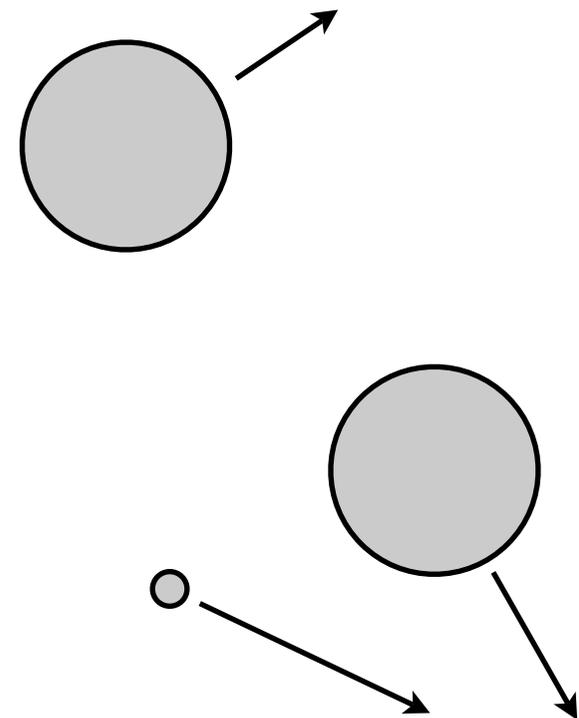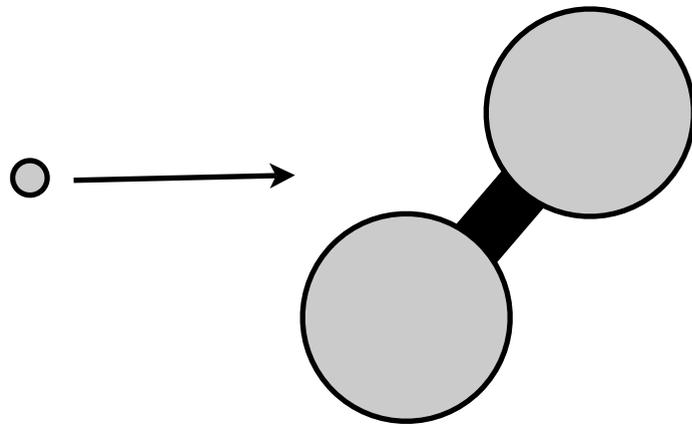
Body-frame and lab-frame

z

x

CM

y
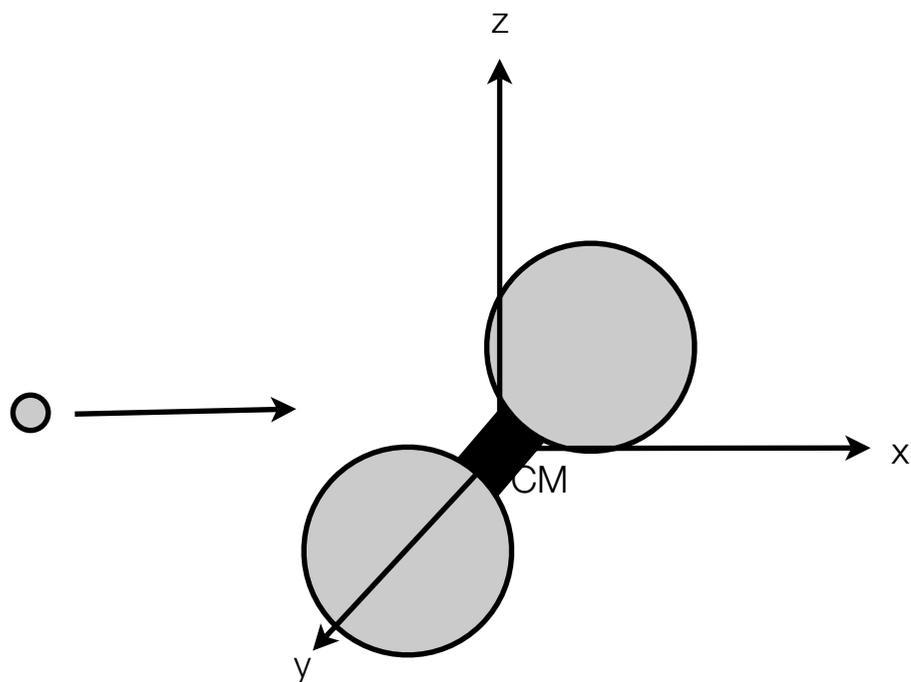
Useful when electron is far from the molecule

z

x

CM

y
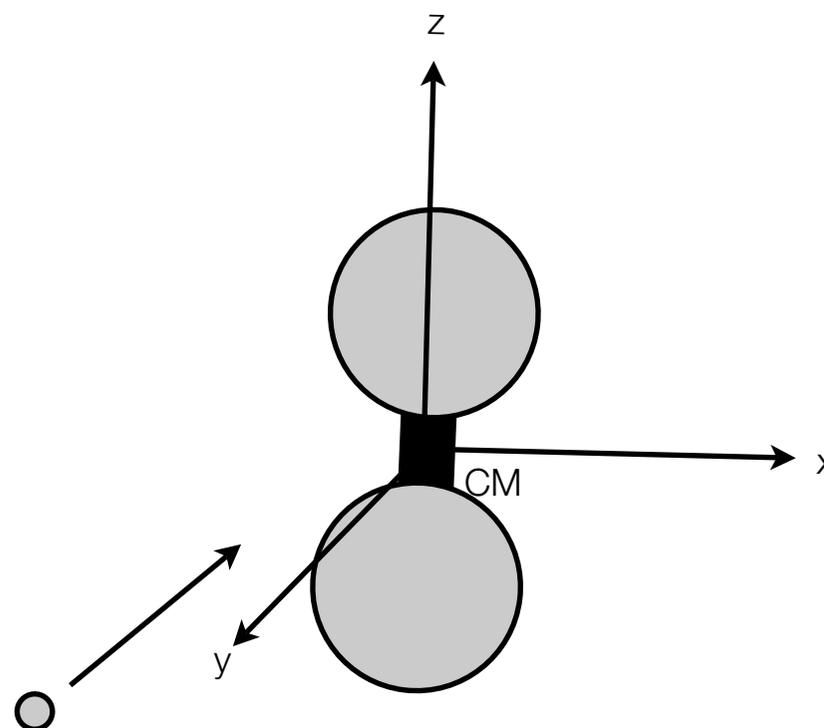
Useful when electron is close to the molecule (N+1 electron system)

Want to know more about the basics of break-up channels: download Han-lectures 1995 from Jaap Snijders from theochem.chem.rug.nl

Elastic scattering

- Elastic scattering is often the only channel considered when studying large molecules

- The Born-Oppenheimer approximation is assumed to be valid (this is not always a good assumption for scattering calculations!)

- Exchange is almost always included as an effective potential, correlation only through an effective polarization potential

- Even elastic scattering is much more involved when dealing with non-spherical systems

Partial waves expansion

- Most scattering methods expand the continuum functions, and often also the optical potential, in partial waves

$$H\Psi_E = E\Psi_E$$

$$\Psi_E = \mathcal{A} \sum_{\substack{\text{target} \\ \text{states}}} \begin{pmatrix} \text{one} - \text{particle} \\ \text{scatteringfunction} \end{pmatrix} \begin{pmatrix} \text{target} \\ \text{eigenfunctions} \end{pmatrix}$$

$$\begin{pmatrix} \text{one} - \text{particle} \\ \text{scatteringfunction} \end{pmatrix} = \sum_{\substack{\text{partial} \\ \text{states}}} \begin{pmatrix} \text{radial} \\ \text{scatteringfunction} \end{pmatrix} \begin{pmatrix} \text{angular} \\ \text{function} \end{pmatrix}$$

- Spherical systems: in the partial wave expansion, every l-value decouples, we have s-wave scattering, p-wave scattering, etc.

- This is not true for non-spherical systems. For example, for linear systems we have waves of Sigma, Pi, Delta, etc. symmetry (compare to MO theory)

- Each angular momentum combination l,m is viewed as a channel, the channels are then coupled using the close-coupling equation

- Since many l,m values need to be included for a correct description of the continuum states and potential, a large set of coupled equations needs to be solved

- Even when doing just elastic scattering!

DNA: state-of-the art

Low-energy electron scattering from DNA including structural water and base-pair irregularities

Laurent Caron[*] and Léon Sanche

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Sherbrooke, Québec, Canada J1H 5N4*

Stefano Tonzani

Nature Publishing Group, 4 Crinan Street, London N1 9XW, United Kingdom

Chris H. Greene

Department of Physics and JILA, University of Colorado, Boulder, Colorado 80309-0440, USA
(Received 4 May 2009; published 13 July 2009)

Elastic scattering of low-energy (0–13 eV) electrons from more realistic models of a DNA base-pair decamer is studied using multiple-scattering theory and T matrices obtained from *ab initio* R-matrix calculations. The models include two types of irregularities usually found in cellular DNA: base-pair mismatch and structural water molecules. Furthermore, we include in our calculation inelastic collisions. It is found that the basic interference patterns observed in the ideal and nonideal (i.e., more realistic) decamers are similar but have different amplitudes and are shifted in energy. Substantial inelastic losses, interestingly, cause pronounced local resonances, which could have an important influence in DNA strand breaks.

DNA bases

- DNA bases can be calculated using R-matrix methods

- Elastic scattering only

Thymine

Cytosine

Uracil

Adenine

Guanine

partial wave expansion
of continuum functions

polarization

correlation

exchange

scattering from effective potential

R

"bound" states of N+1
system
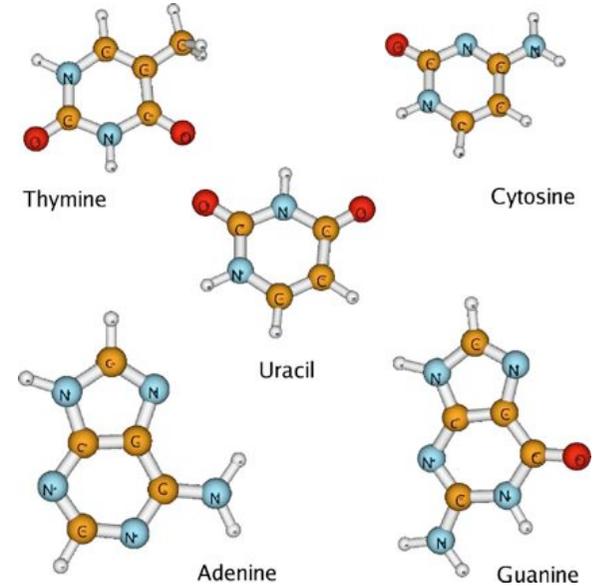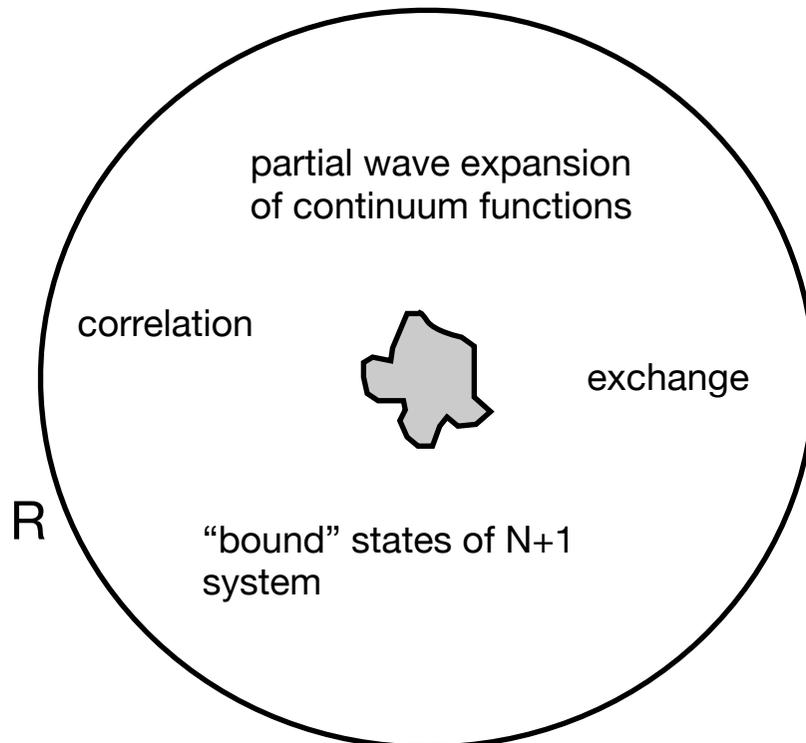
DNA bases

- Exchange and polarization (correlation) effects are included using an effective potential

- LDA exchange potential is used

- Polarization-correlation potential is also based on DFT

  - The correlation potential LYP is used to include polarization and "correlation"

Thymine

Cytosine

Uracil

Adenine

Guanine
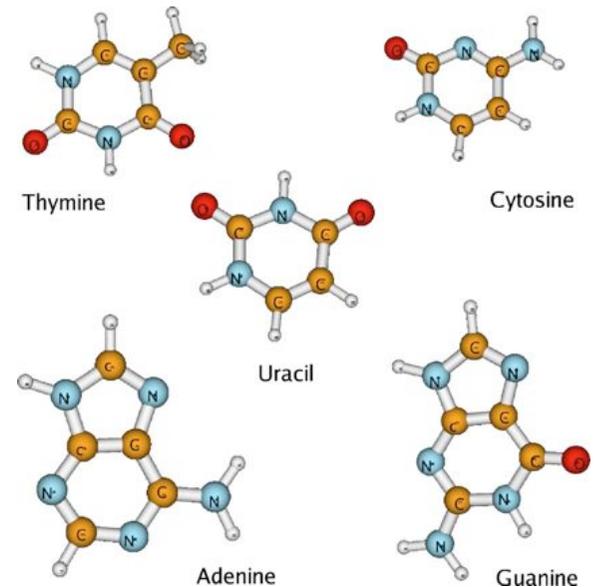
DNA bases

- Target states are obtained from HF

- Finite elements: basis functions consisting of simple polynomials defined only in very small sectors. Continuity between sectors

Thymine

Cytosine

Uracil

Adenine

Guanine
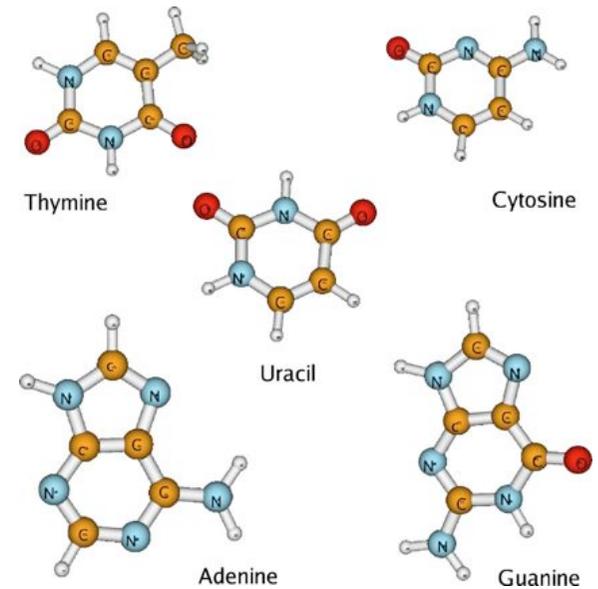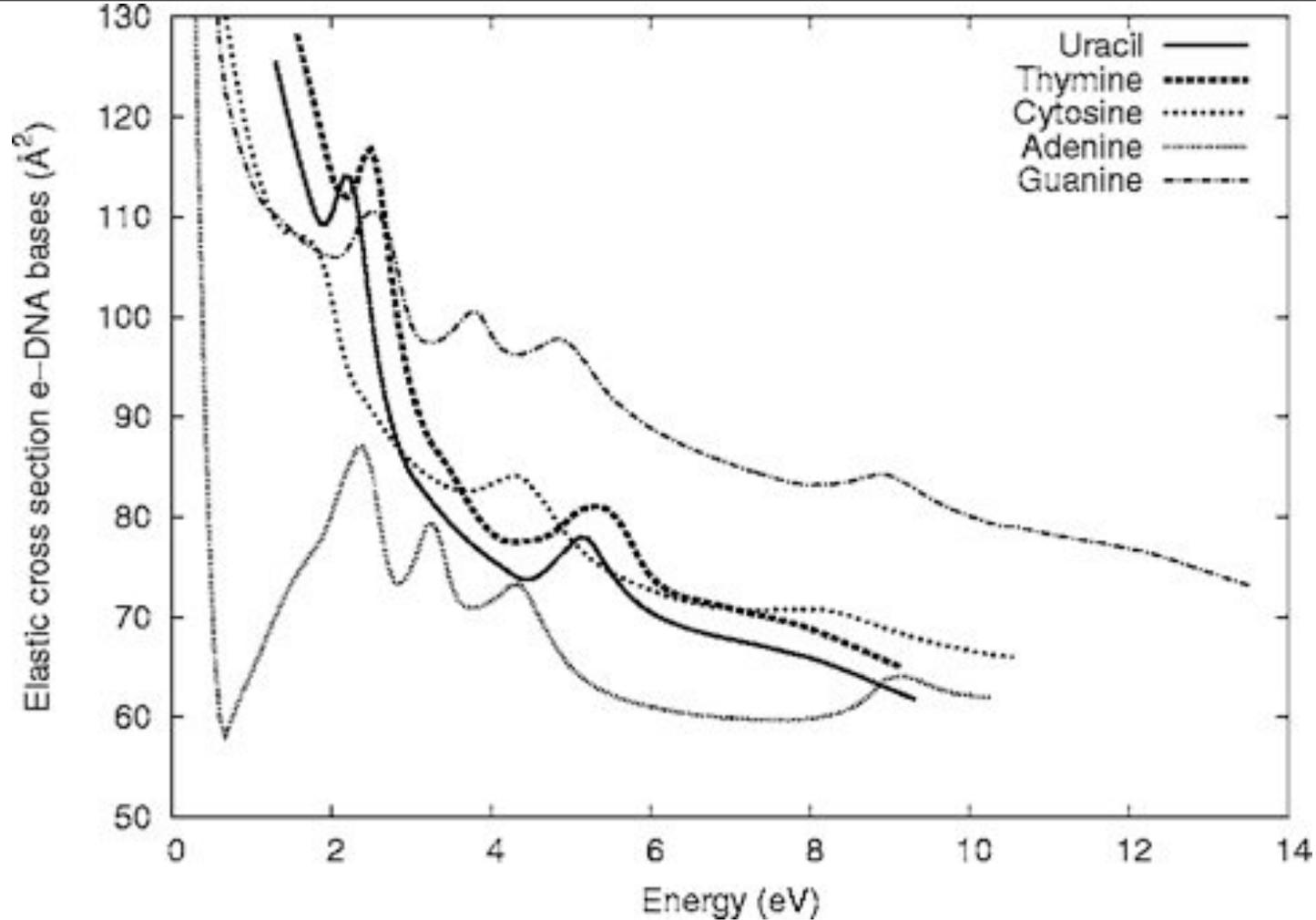
- Resonances are mainly shape resonances where an electron is captured in one of the low-lying unoccupied states of the molecules

- These resonant states might be precursors to dissociation of the molecule

- From their results C-C and C-N cleavage due to these resonances seems possible reasonable

S. Tonzani and C. H. Greene. Low-energy electron scattering from dna and rna bases: Shape resonances and radiation damage. J. Chem. Phys. **124**:054312, 2006.

Backbone

- The same techniques have been used to study models of backbone sugar and phosphate units
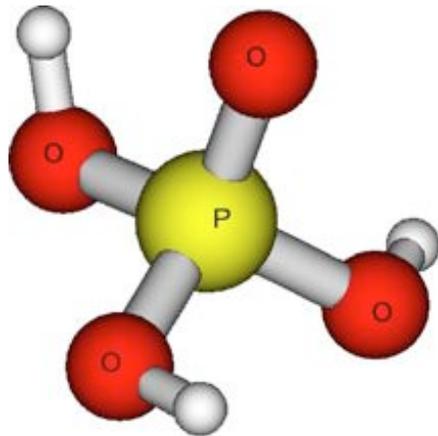
Phosphoric acid
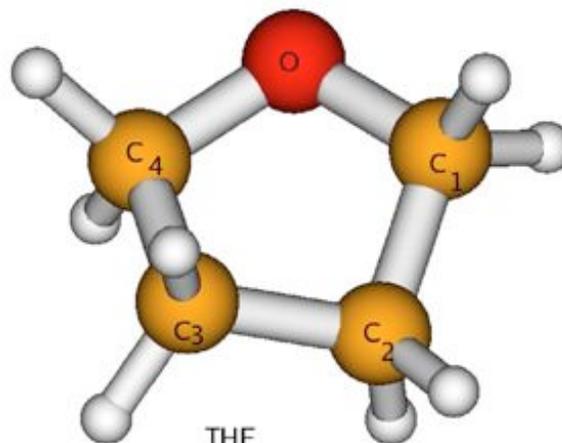
THF
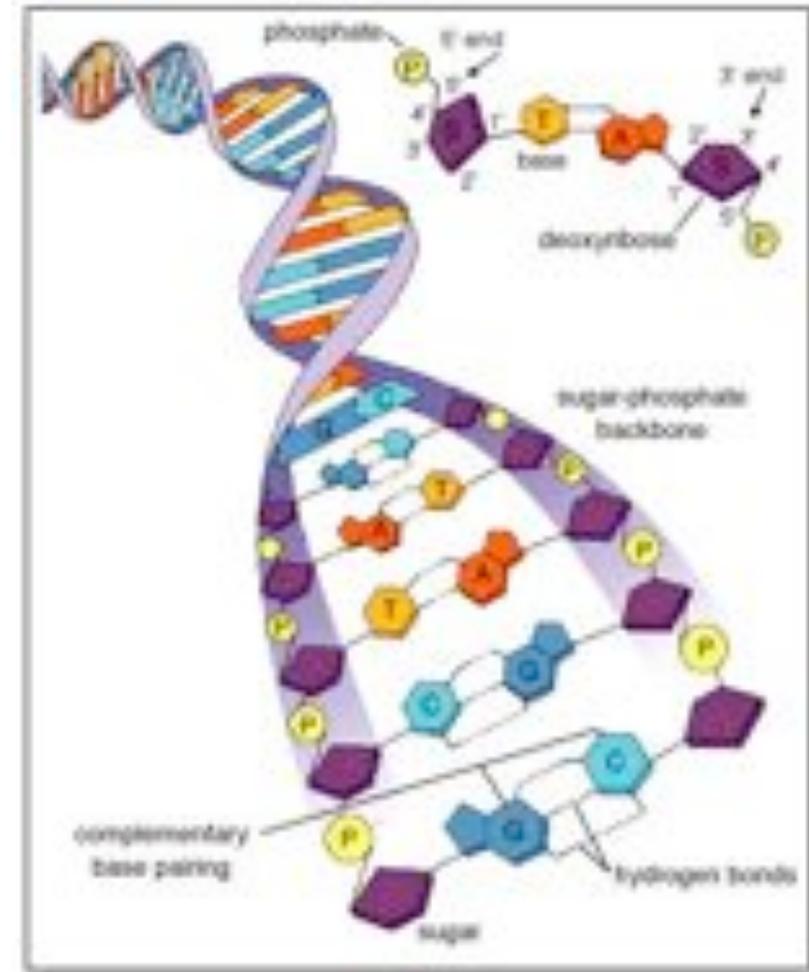
Backbone
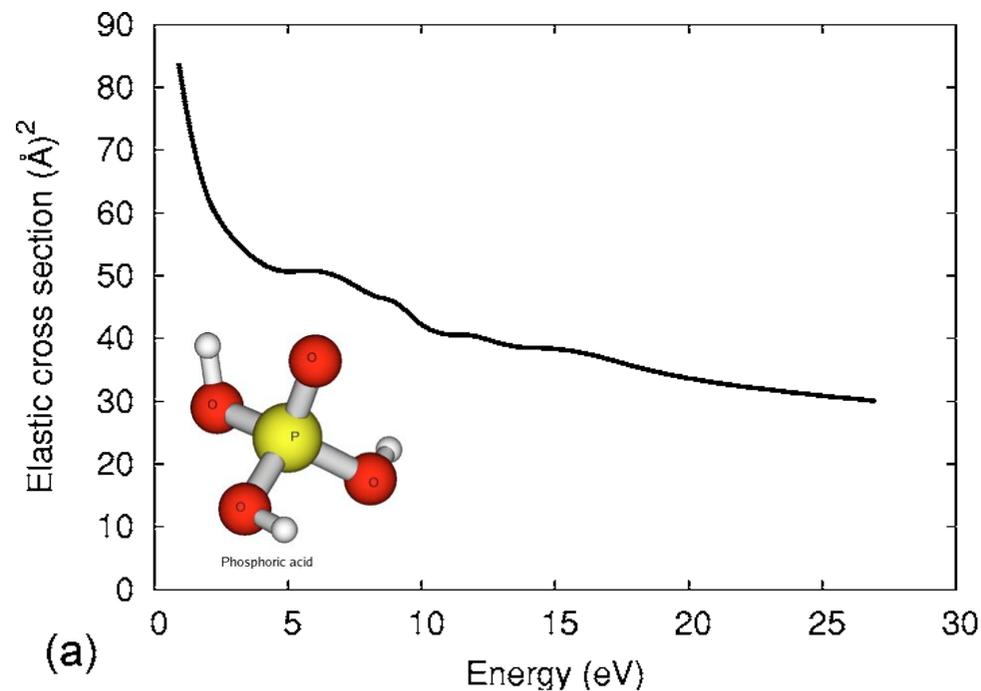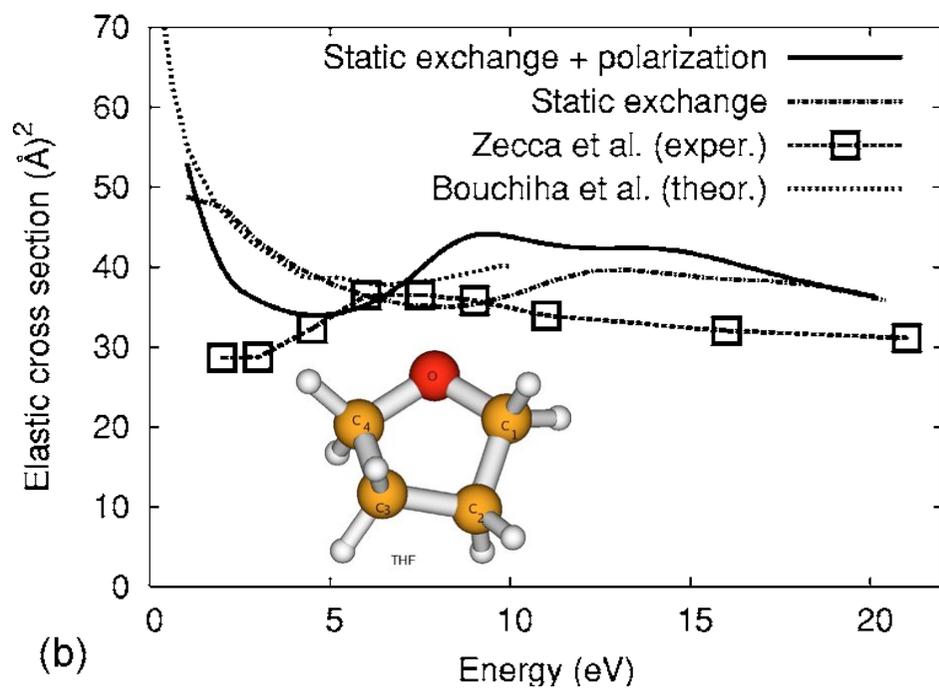
- Again TG find shape resonances that can be precursors to ring breakage (THF)
- In phosphoric acid the shape resonances are very broad and are unlikely to contribute

S. Tonzani and C. H. Greene. Radiation damage to dna: electron scattering from the backbone subunits. J. Chem. Phys. **125**:094504, 2006.

Base pair decamer with (some) water

- To study this large system, multiple scattering theory is applied

- The total (very complicated) potential is decomposed in many local potential that do not overlap

- A Muffin-Tin like potential is obtained from which the electron is scattered

- Information from the DNA base calculations is used to generate the potential
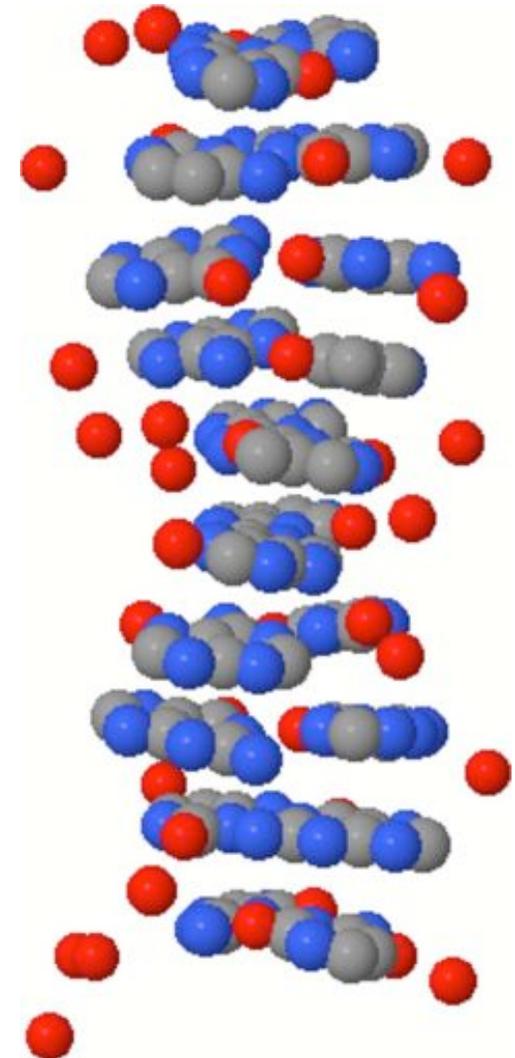
FIG. 1. (Color online) Side view of the decamer. The oxygen atoms of the retained water molecules appear as isolated spheres.

Base pair decamer with (some) water

- Two incident electron directions were studied, perpendicular to the decamer axis

- Electron loss is modeled using an imaginary part in the potential

- The sharp resonances could play an important role in strand breaking because they could efficiently funnel electrons to the DNA backbone.

- In particular, large energy losses to electronic excitation create additional very low-energy electrons, which have a propensity to transfer to the DNA backbone and break the C-O bond i.e., break the DNA chain
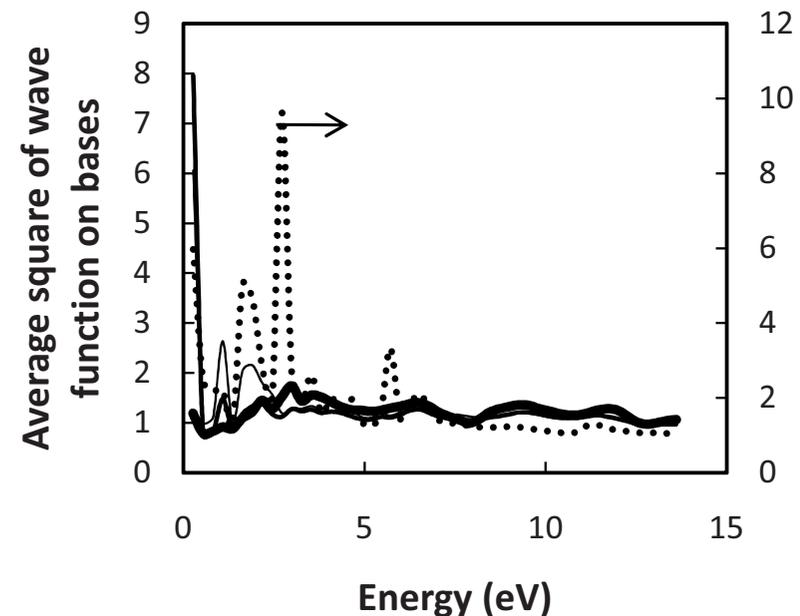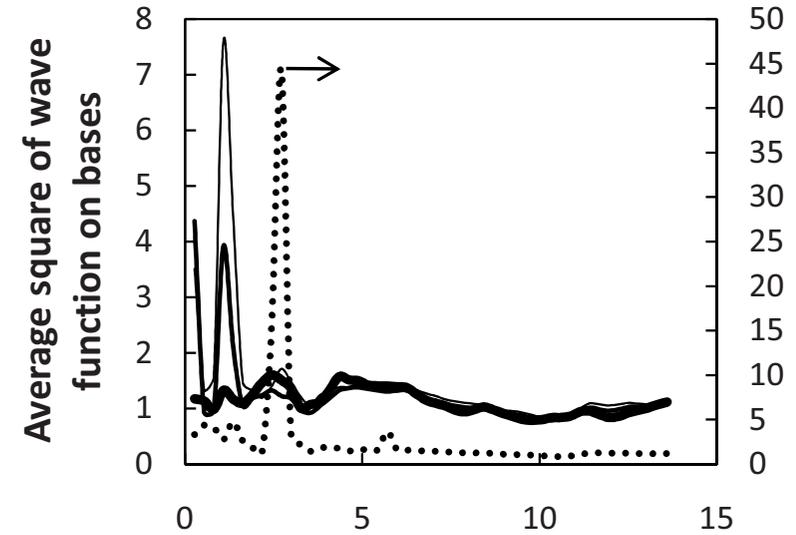
Molecules with DFT: outlook

- Off-center atoms need different cutoff factor

  - analytic integration is more difficult

- Two center integrals need to be implemented

- TDDFT scattering theory for molecules needs further development

off-center atoms

two-center integrals

Summary

$$k = \sqrt{2E}$$
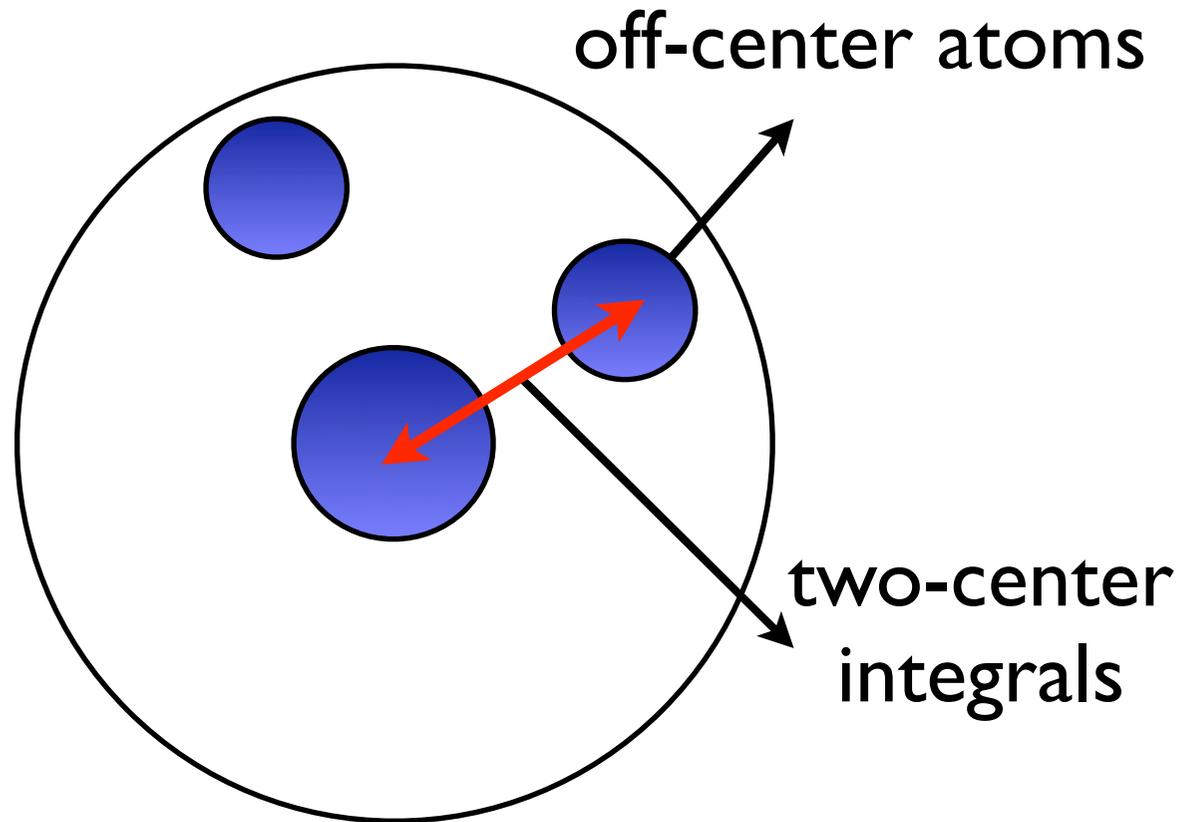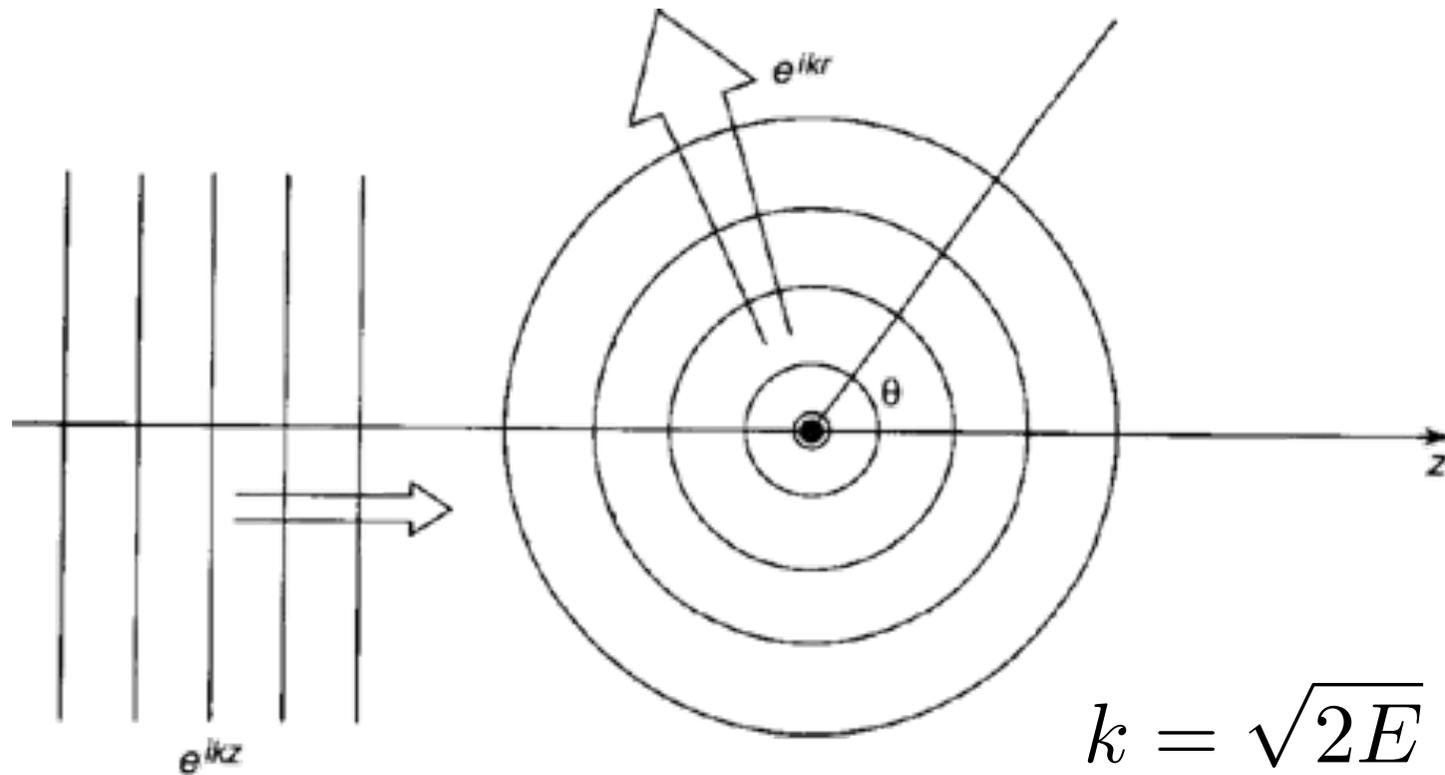
$$\psi(r) = e^{ikz} + f(\theta, \phi)\frac{e^{ikr}}{r} \quad r \to \infty$$

- We are looking for a solution of the SE with as boundary condition an incoming wave plus an outgoing spherical wave

Scattering from potentials

- We can obtain cross-section from knowledge of the scattering amplitude *f*

$$\sigma = \sum |f|^2$$

- The scattering amplitude itself can be obtained from the phase shifts

$$f(\epsilon) = \sum_{l=0,1} i\epsilon^l e^{i\delta_l} \sin(\delta_l) \qquad \text{1D}$$

$$f(\theta) = \sum_{l=0}^{\infty} \frac{2l+1}{k} e^{i\delta_l} \sin \delta_l \, P_l(\cos\theta) \qquad \text{3D radial}$$

- Obtain scattering information from matching the wave function at the boundaries of the (short-ranged) potential

- The same results can be obtained by placing a 1D or 3D spherical potential in a box

Practical calculations: wave-function

- One often approximates the wave function by the following expansion

$$\Psi_k = \mathcal{A} \sum_{ij} a_{ijk} \Phi_i^N \eta_{ij} + \sum_m b_{mk} \Phi_m^{N+1}$$

Anti-symmetrizer

Target functions

1-electron continuum functions

(N+1) electron short-range functions (Gaussians)

- This expression can be used as a trial wave function in a variational calculation

- Levels of approximation: static, static-exchange, static-exchange plus polarization

- Exchange is usually approximated by a local potential

Practical calculations: wave-function

- R-matrix

partial wave expansion
of continuum functions

polarization

correlation

exchange

scattering from effective potential

R

"bound" states of N+1
system
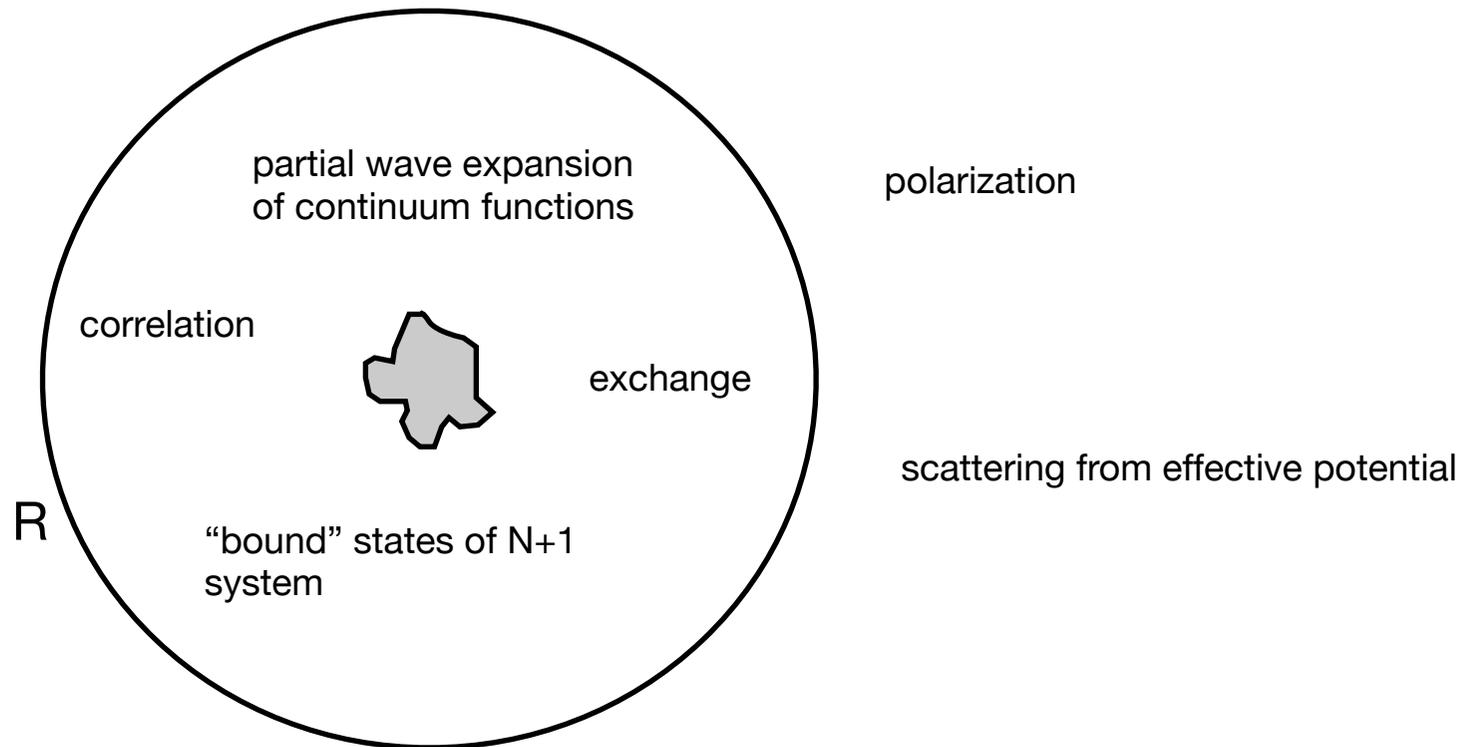
Practical calculations: TDDFT

- We start from an (N+1)-electron ground state DFT calculation in a box

- Excite electron into the continuum with TDDFT and obtain phase shifts

- At the moment only atoms, but many-electrons can be treated in principle

- BSTO basis set allows for implementation in QC codes (ADF)

- Future: molecules -> will TDDFT become the new state-of-the-art for large molecules?

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NWO

Nederlandse Organisatie voor Wetenschappelijk Onderzoek