

TIME-DEPENDENT DENSITY-FUNCTIONAL THEORY FOR ELECTRON-ATOM SCATTERING: FINITE BASIS SET CALCULATIONS

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Introduction

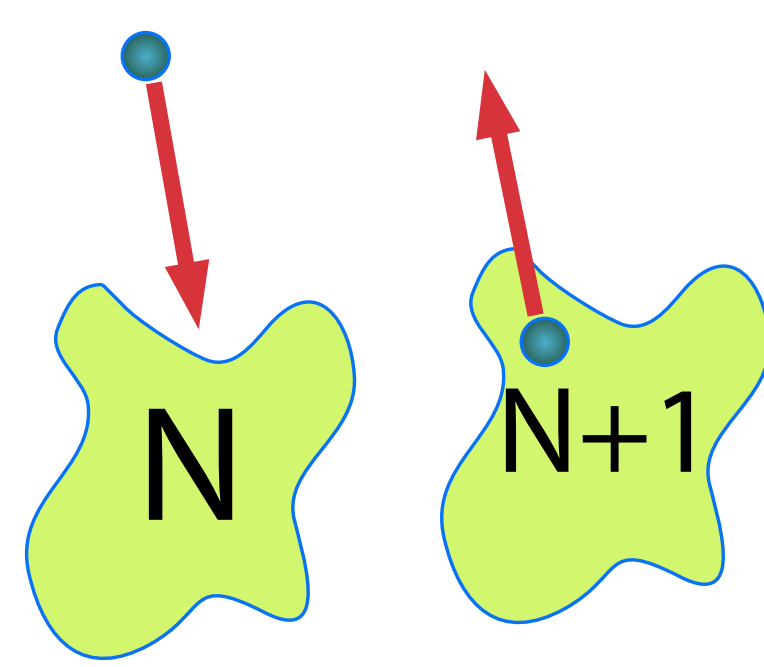
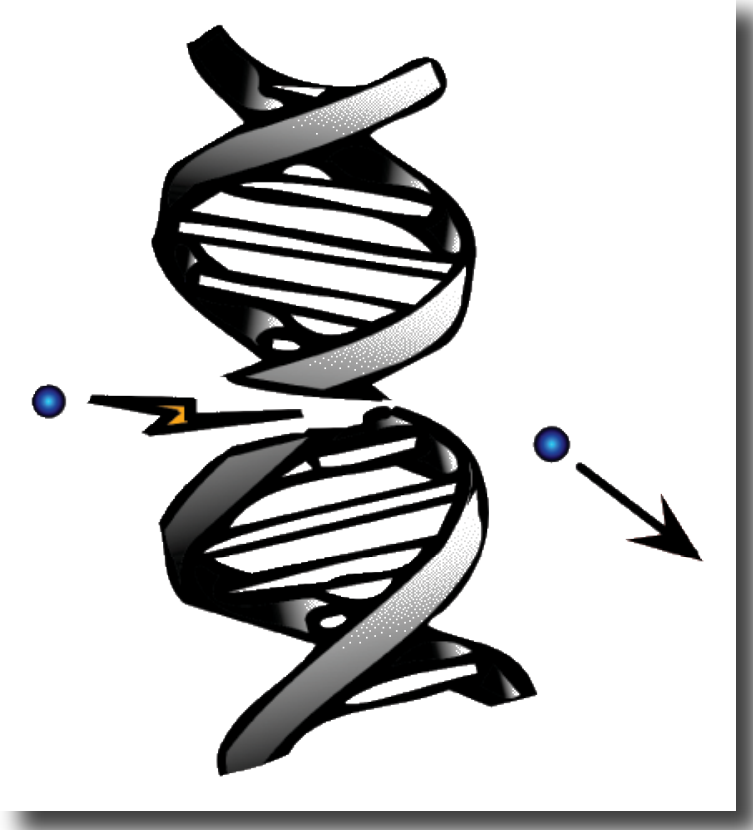
Experiments by Sanche et al. [1] have shown that very low energy electrons (3-20 eV) are capable of inducing DNA strand breaks. Present day ab initio scattering methods are unable to describe large DNA fragments because of high computational cost.

(TD)DFT is a computationally much cheaper method. In collaboration with prof. Kieron Burke (UCIrvine, USA) a scattering method for DFT is being developed.

Scattering with (TD)DFT

The correct procedure is to start from a system that combines the target and the scattering electron [2]. That is, we start from a situation where the electron is bound to the target system, or resides in a resonant state of the target.

We then excite the added electron into the continuum using TDDFT, and calculate the excitation energy. If our target is an atom, and the (N+1)-electron system has a short ranged potential, we can place the atom in a box and obtain the phase shift from the excitation energies.



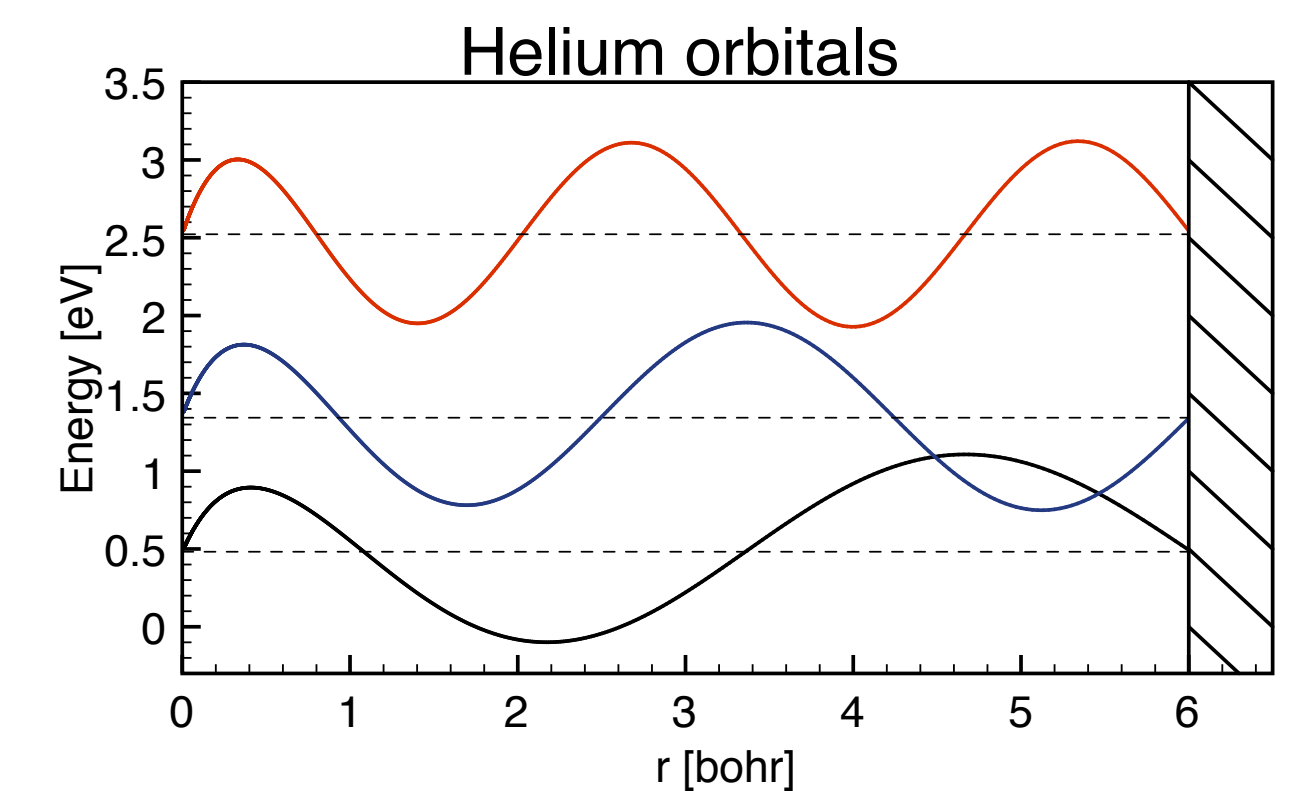
Atom in a cavity

Putting an atom inside a hard sphere cavity discretizes the continuum. Each positive energy state obtained corresponds to true continuum states, up to the wall radius R .

The scattering phase shift can then be obtained from these "continuum" orbitals, for a long ranged potential such as He, from:

$$\tan \delta_{nl} = -\frac{F_l(-1/k_n, k_n R)}{G_l(-1/k_n, k_n R)}$$

where F and G are Coulomb functions and $k_n = \sqrt{2E_n}$

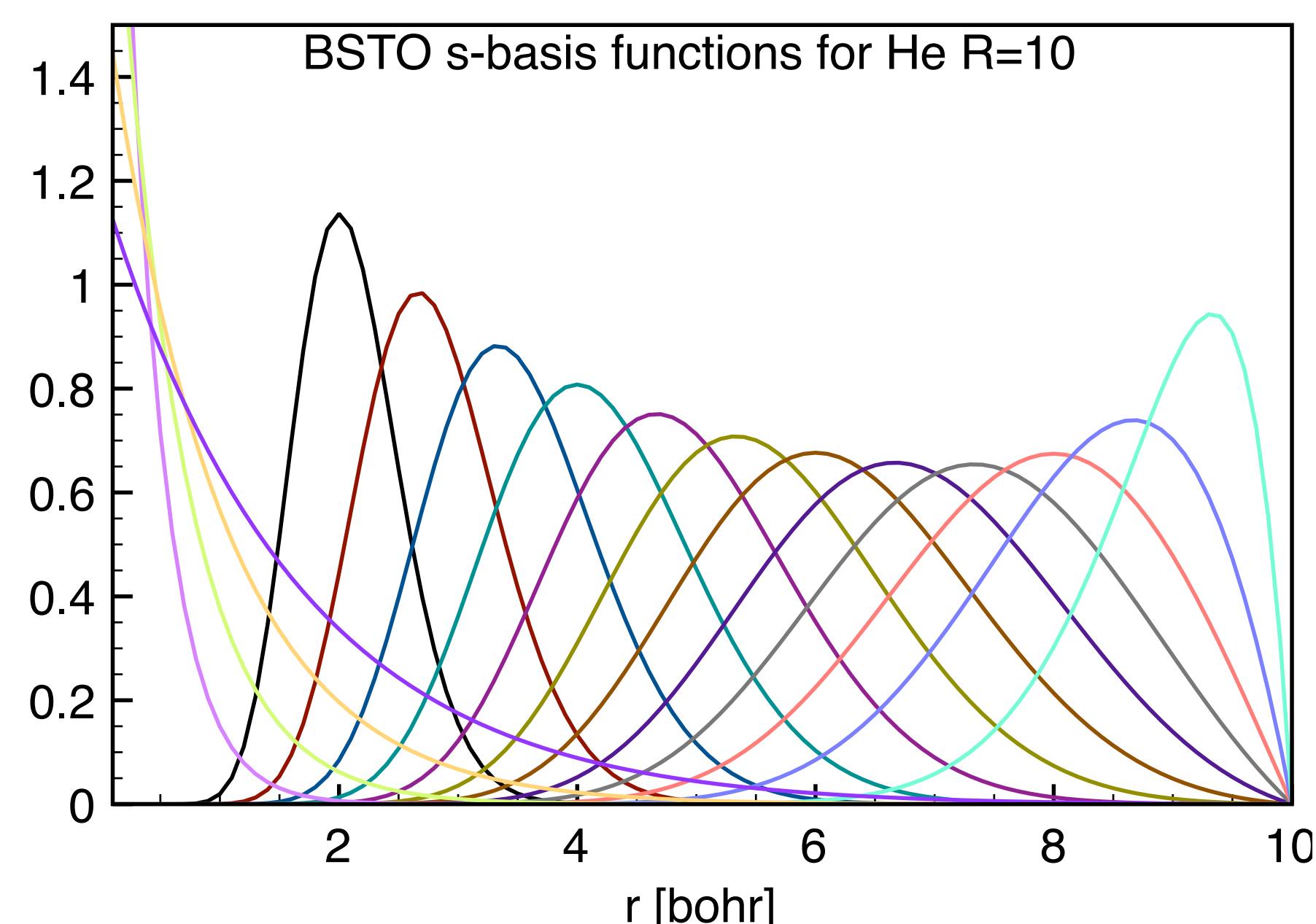


BSTO basis set

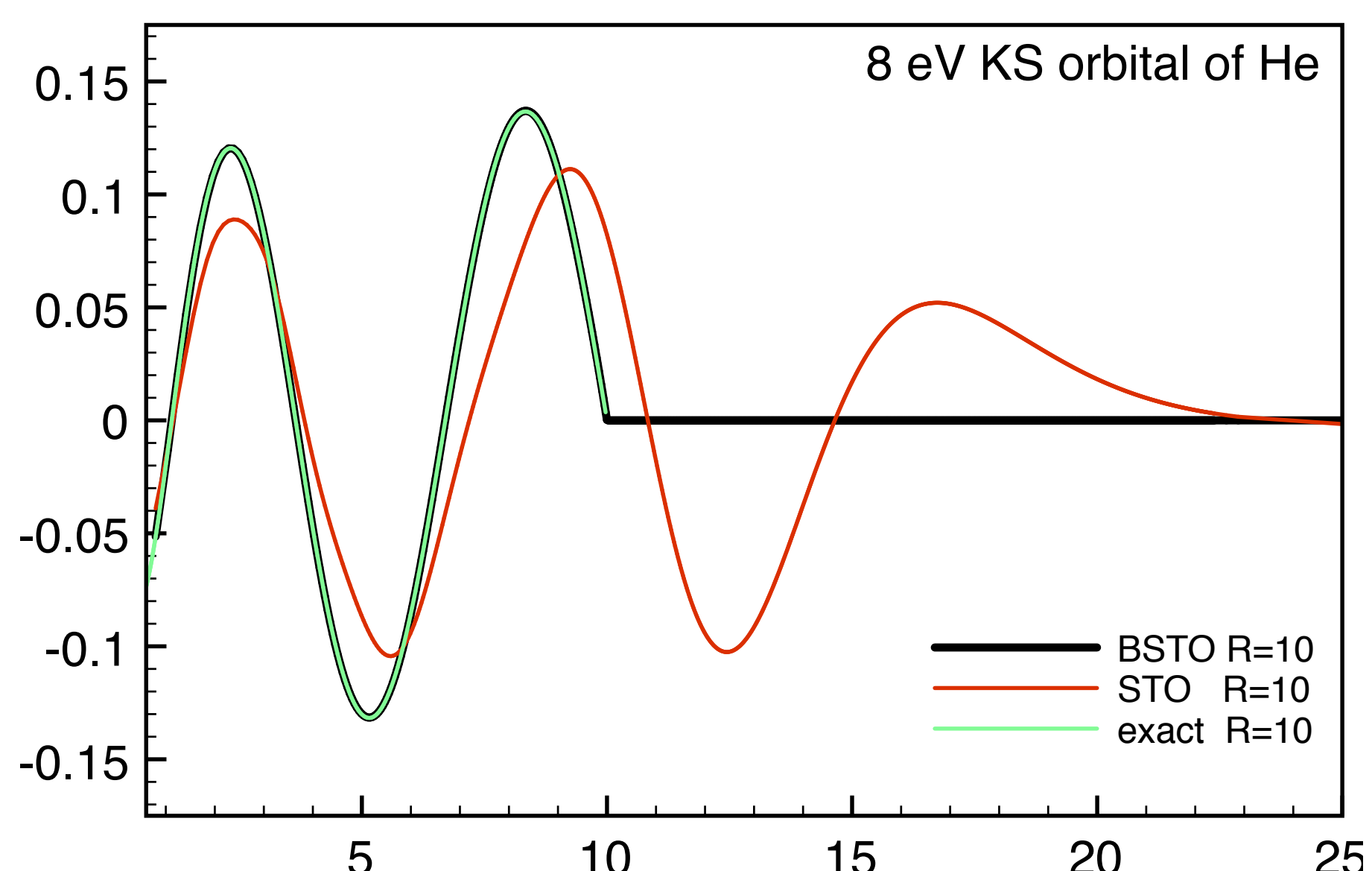
Most quantum chemistry codes use some sort of finite basis set. To introduce the hard wall cavity, we multiply the radial part of the basis functions (Slater type orbitals, STO) with a pre-factor that becomes zero at the wall:

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

A typical boundary STO (BSTO) basis set corresponding to a wall placed at $R=10$ is shown in the figure below:

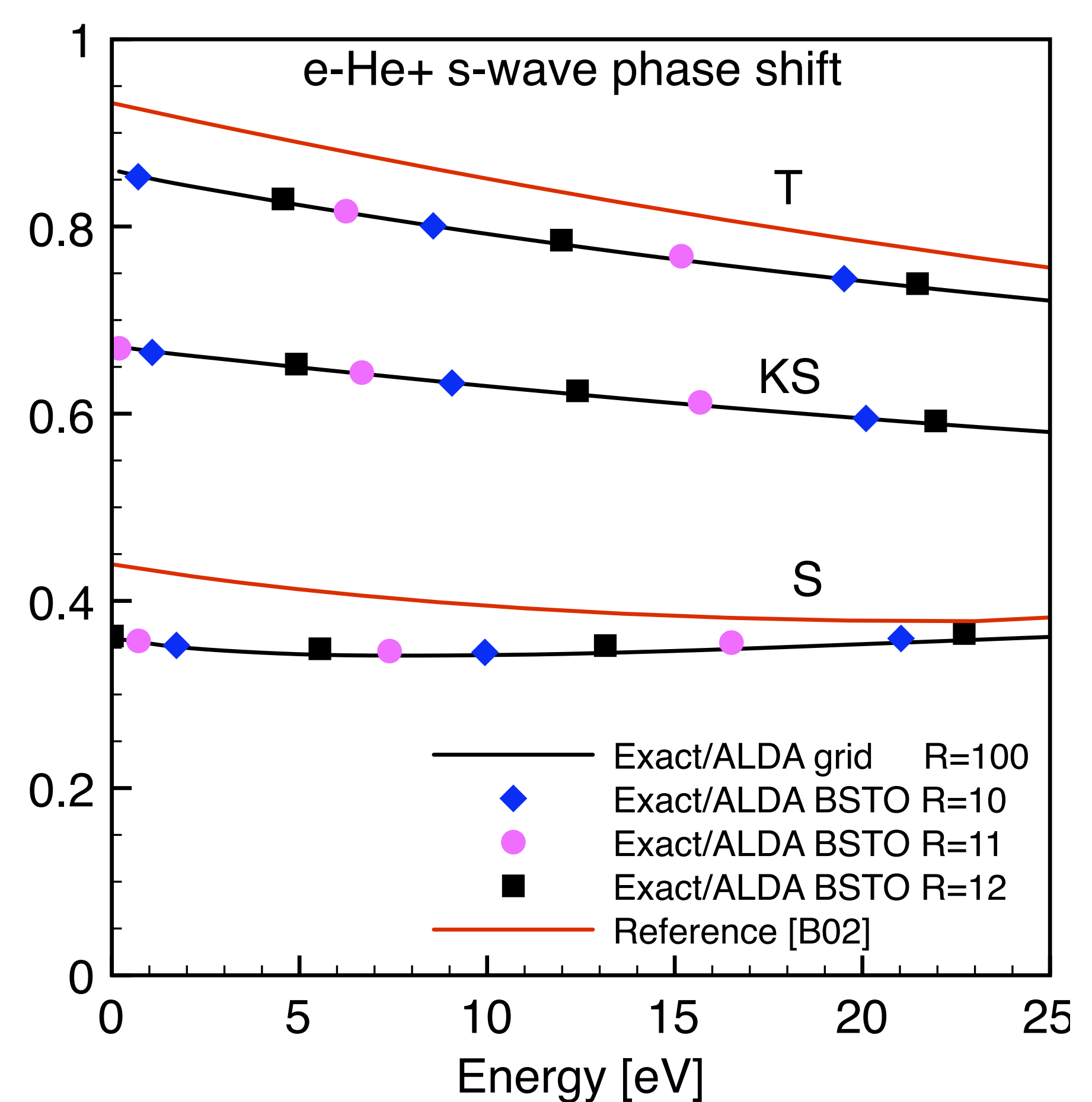


The pre-factor is essential as can be seen in the figure below. The red line is obtained by using an STO basis set with the same exponents as in the basis above, but without the pre-factor. The BSTO basis gives the exact orbital:



Phase shifts

The phase shifts obtained from a suitably chosen, large BSTO basis set, are equal to the phase shifts obtained using a grid code with a wall placed very far away (the "exact" (TD)DFT results). The finite basis set method does not allow the cavity to be too large, to keep the basis set size manageable and to avoid linear dependency problems. Therefore multiple calculations at different smaller wall sizes need to be performed to fill in the curves.



Conclusion

The phase shift for low-energy electron-atom scattering obtained with TDDFT is remarkably accurate. The atom is placed in a hard-wall cavity to obtain the continuum KS orbitals as pseudo-states.

A finite size basis set with a boundary pre-factor is able to reproduce the exact TDDFT results. Since only small wall radii can be used, different wall sizes are needed to fill in the phase shift curves.

References

- [1] B. Boudaïffa, P. Cloutier, D. Hunting, M. A. Huels, and L. Sanche, *Science* 287, 1658 (2000)
[2] A. Wasserman, N.T. Maitra, and K. Burke, *J. Chem. Phys.* 122, 144103 (2005)
[B02] A. Bhatia, *Phys. Rev. A*, 66, 2002.

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Relevant papers:

- M. van Faassen, A. Wasserman, E. Engel, F. Zhang, and K. Burke, "TDDFT calculation of e-H scattering", *Phys. Rev. Lett.* 99, 043005 (2007)
M. van Faassen and K. Burke, "Time-dependent density functional theory of high excitations: To infinity, and beyond", PCCP to be submitted
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M. van Faassen, "TDDFT for atoms in cavities and electron-atom scattering phase shifts: a finite basis set method", in preparation