Scientific Report for the Short Term Scientific Mission

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Purpose of the visit

The visit at University College London was focused on theoretical study of nitric oxide (NO) molecule using the R-matrix method. Particularly, we have been interested in parameters (positions and widths) of the lowest lying resonances. Large-scale quantum-chemical and scattering calculations of these parameters were already carried out ([1], [2]). Our purpose was to carry out computationally less demanding calculations and to investigate obtained resonance parameters dependent on a choice of the quantum-chemical basis, number of electronically excited states of the target and the R-matrix radius.

Description of the work carried out during the visit and main results

We carried out most of the calculations at equilibrium geometry at the internuclear separation 2,1747 bohrs. The quantum chemistry method employed was Configuration Interaction with Hartree-Fock orbitals. We began the calculations with the standard *DZP* basis and subsequently proceeded to the *aug-cc-pVTZ* basis and to a modified (as suggested by [3]) *aug-cc-pVTZ* basis which yielded correct order of electronically excited states of the molecule. This modified basis was the *aug-cc-pVTZ* basis augmented by two additional sets of s and p orbitals built from the two most diffuse valence s and p functions.

Basis	Number of target states	R-matrix radius [Bohrs]	E_{res} [eV]	Γ_{res} [eV]
DZP	9	10	1,97	0,5411
aug-cc-pVTZ	9	10	2,05	0,3891
aug-cc-pVTZ	15	11	2,14	0,2505
Modified aug-cc-pVTZ	15	12	1,95	0,4418
Modified aug-cc-pVTZ	40	12	1,02	0,1975

Table 1: Calculated parameters of the $^3\Sigma^-$ resonance

Scattering calculations were performed using the Close Coupling method. Four electrons were frozen in the calculations. Number of CAS virtuals was 2 for all calculations except the last with 40 states, where it was increased to 3. The list of performed calculations and calculated parameters of the lowest lying $^3\Sigma^-$ resonance is given in Table 1.

We found that increasing the R-matrix radius from 10 bohrs to 12 bohrs is necessary in order to remove some of the artificial structures of eigenphase shifts. This was especially true for the $^1\Delta$ resonance. In this case, artificial parts of eigenphase shifts makes it difficult to locate the physical resonance.

Results from the calculations of [1] and [2] predict the following parameters of the $^3\Sigma^-$ resonance:

E_{res} [eV]	Γ_{res} [eV]	Model
0,46	0,17	Analytic continuation ([1])
0,43	0,16	Complex Kohn ([1])
0,90	0,18	R-matrix ([2])

Table 2: Resonance parameters for the $^3\Sigma^-$ resonance

We see from the Tables 1 and 2 that the results of our last calculation for 40 excited states of the target are close to the previous R-matrix calculations from the Table 2. This is not surprising since polarisation of the target is well described in our calculations. But we cannot state from our calculations with 15 and 40 states that the width and the position of the resonance are already converging because proof of this statement would require calculations with more states of the target. This was not possible to complete during my stay at UCL because of longer computer time needed to answer this question.

Finally the potential curve of the neutral molecule in the *DZP* basis was calculated (Fig. 1) in a range of relevant internuclear separations.

References

[1] Zhiyong Zhang, Phys. Rev. A **69**, 062711 (2004)

[2] Jonathan Tennyson, J. Phys. B: At. Mol. Phys. **19** (1986) 4025-4033

[3] Huancong Shi, J. Chem. Phys. **125**, 104311 (2006)

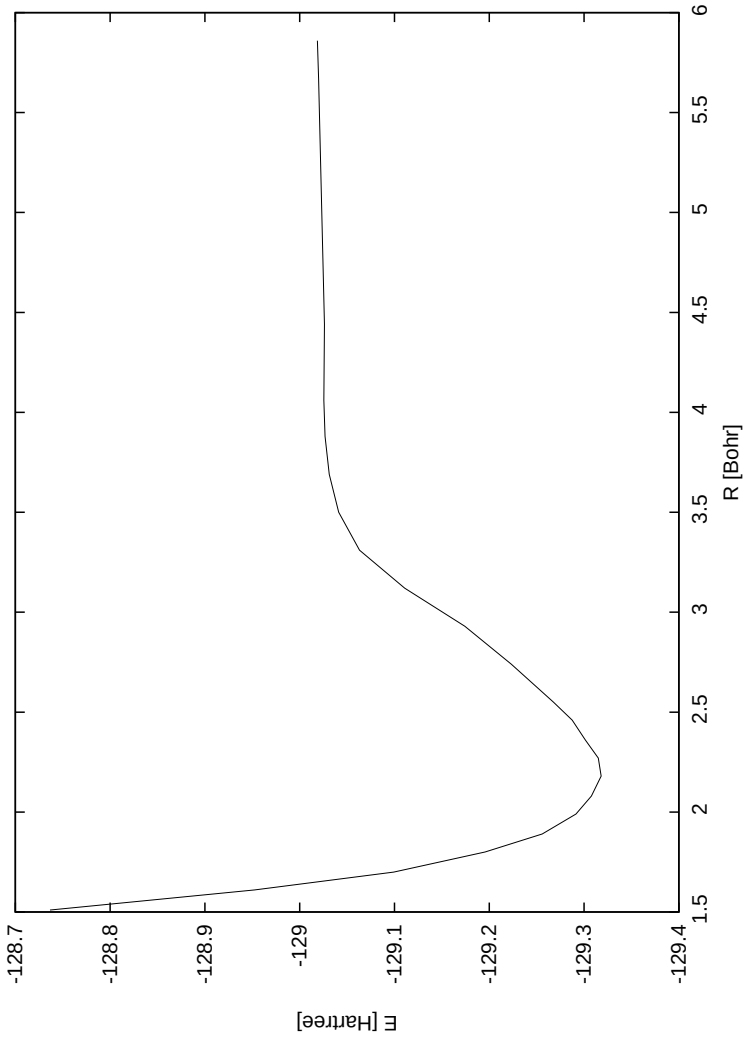

Figure 1: Potential of the neutral NO molecule