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Thesis Changes Log

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PhD Program: Materials Science and Engineering

Title of Thesis: Accurate ab initio evaluation of the interatomic potentials and long-range coefficients
Supervisor: Prof. Alexei A. Buchachenko

The thesis document includes the following changes in answer to the external review process.

Answers to the corrections and questions made by Prof. T. Wright (University of Nottingham)

The corrections suggested in the annotated version of the Thesis were carried out. In particular, in Section 2.5.5, I kept the symbols and subscripts used by Stanton (J. F. Stanton, *Why CCSD(T) works: a different perspective*, Chem. Phys. Lett., **281**, 130–134 (1997); doi: 10.1016/S0009-2614(97)01144-5) for consistency with the Reference.

In his report, the Reviewer asked five questions and requested to discuss them during the defense. In compliance with his request, these questions will be answered at the viva. For the awareness and convenience of the reader, these are listed below:

Q1. How is the CP correction undertaken with bond functions, and is there an optimal place to put these in a heteronuclear system?

Q2. How does long-range electronic structure relate to that at R_e for open-shell systems? E.g. for N...N going to N2?

Q3. Is it always clear what electronic states have been selected, e.g. in the U+-RG calculations, when the 4f electrons are explicitly considered.

Q4. What are the implications of neglecting multireference effects?

Q5. Would spin-orbit effects help reliability in some cases?

Answers to the corrections and questions made by Prof. S. Levchenko (Skolkovo Institute of Science and Technology)

Q1. "with the long-range coefficients C_n^AB [9,10]" – discuss how the cutoff R between short- and long-range is defined
Corrected in the Thesis: "*In a potential energy curve, the long-range region described by the form (1.1) correspond to the asymptote of the curve*"

Q2."and omitted forces of the non-Coulomb origin" – clarify which ones

Corrected in the Thesis: *"(e.g. forces rising from the overlap of the electron clouds)"*

Q2. *"However, in the ambit of atomic response properties, atomic approaches, such as that combining Configuration Interaction method and Many-Body Perturbation Theory (CI-MBPT) [23] turned out to be more flexible and more easily customizable for specific systems, having the possibility even to embody empirical corrections (see Ref. [23])." – why is this good? don't we want a black box method without any parameters to get predictive power?*

Empirical corrections, and, generally, all corrections made *a posteriori*, are good, since in many cases "raw" ab initio methods do not attain the accuracy required to support experimental accuracy. This is particularly true in the field of cold and ultracold physics. This problem is exemplified in Chapter 4 of the Thesis, where raw ab initio data are not accurate enough to comply with the accuracy required by photoassociation spectroscopy experiments.

"they are usually empirical, retrieved from first-principles ab initio calculations or from experimental data [24,29]." – if they are retrieved from ab initio calculations, they are not empirical

Here "empirical" is meant is the sense of the derivation, rather than in the sense of reference information. However, to avoid misleading terms, the word "empirical" has been replaced by the word "phenomenological".

Q3. *Equation 2.6 – explain what R_lk(a) is*
Corrected in the Thesis.

Q4. *"the redistribution of charge under application of an external electric field depend on the direction ..." – "...depends..."*
Corrected in the Thesis.

Q5. *"The Thesis will mostly discuss systems where charge distribution is isotropic or, however, anisotropy is negligible." – "however" seems strange in this context*
Corrected in the Thesis.

Q6. *"According to Time-dependent Perturbation Theory, the wave function should be ..." – this form of wave function has nothing to do with perturbation theory, any wave function can be expressed in this way since the basis of psi_k is complete; by the way, please explain in the text what psi_k are.*
An explanation regarding ψ_k was added. Moreover, the suggestions regarding the correction of the related paragraph were applied in the Thesis.

Q7. *"The frequency \omega is high enough to make the field gradient and the higher derivatives negligible." – you did not introduce \omega; also, explain what \omega_k and \omega_kn are*
The meaning of ω_k and ω_{kn} were explained after the suggestion of the Reviewer.

Q8. *"In facts" -> "In fact"*
Corrected in the Thesis.

Q9. *Around Eq. 2.51 – please remind what alpha_{alpha gamma}(i omega) are*
After the Reviewer's suggestions, I added a short phrase in the Thesis, where I remind the reader that $\alpha_{\alpha\gamma}(i\omega)$ [in the Thesis generalized as $\alpha_{\lambda\nu}^{X}(i\omega)$] refers to the dynamic polarizability tensor of the species X.

Q9. *"Thus, there is no system with the long-range interaction growing faster with the distance." – confusing wording: the interaction is decaying with increasing distance*

The sentence was deleted to suppress any source of misleading.

Q10. *"When the distance between the interacting species A and B is larger than the wavelength lambda_0, corresponding to the characteristic adsorption frequency of the perturbed species under study" – did you mean absorption frequency for electronic excitations? please clarify this sentence*
The sentence was clarified after the Reviewer's suggestion in the Thesis. λ_0 stands for the wavelength corresponding to the characteristic atomic absorption frequency of the perturbed species. The sentence refers to A. J. Stone, *The Theory of Intermolecular Forces*, (Oxford University Press, Oxford, 2013) and, in particular, to H.B.G. Casimir and D. Polder, *The influence of Retardation on the London van der Waals forces*, Phys. Rev. **73**, 360 (1948); doi: 10.1103/PhysRev.73.360, where it is reported "*an influence of retardation on the interaction is to be expected as soon as the distance between the particles becomes comparable to the wavelength corresponding to the atomic frequencies*"

Q11. *Eq. 2.62 – it should be a determinant*
Eq. (2.62) represents the first solution ever proposed to solve Hartree-Fock equations. It was first introduced by Hartree and after him bears the name "Hartree product" (see, for instance, D. R. Hartree, *The Calculation of Atomic Structures*. New York: John Wiley & Sons (1957). LCCN 57-5916). This solution has turned out to be an unphysical approximation disregarding the permutation symmetry ~~for~~ of the exact wavefunction. Thus, Slater Determinant were later introduced. In the related sections, I wanted to explain, step by step, the mathematical strategies that finally led to develop Hartree-Fock method. Thus, to describe Slater Determinant and explain the reasons for the determinantal form of the wavefunction, I needed to introduce its nowadays obsolete *"ancestor"*.

Q12. *"It should be noticed" -> "it should be noted"*
Corrected.

Q13. *"finite field CCSD(T) method" – this method was not introduced*
Finite field (FF) method was introduced in Section 2.6.1, among the Coupled Cluster methods for electric properties, as a strategy to compute static electric properties. Its implementation does not depend on the specific method by which the wavefunction is computed, as it is an application of the Hellmann-Feynman theorem. Thus, the information and results described in the abovementioned section are general and apply to any level of theory.

Q14. *"As the difference between scalar relativistic approximations (X2C vs. DKH2) should be very small (See Chapter 3, Section 3.3), This mismatch is due ..." – "..., this mismatch..."*
Corrected.

Q15. *Chapter 5 discusses anisotropic interactions, but no calculations of such interactions were done. It should be clearly discussed why this is so challenging compared to presented tests. Why the combinations rules were not actually tested for anisotropic interactions?*
Our combination rule (CR) was not tested on anisotropic interactions, as we did not find good representative examples of this kind. However, extension to anisotropic interactions is theoretically straightforward: one may use the CR to retrieve the scalar and tensor components of the dispersion coefficients. Overall, generalizations to anisotropic case(s) were avoided in the Thesis due to their cumbersome presentation.

Q16. *"electric properties of atoms" – I don't think this is a proper term; the correct one would be "electronic properties"*
Properties of atoms related to the response to an external electric field are conventionally named *electric properties*. For instance: A.J. Sadlej, *Medium-sized polarized basis sets for high-level correlated calculations of molecular electric properties. II. Second-row atoms Si–Cl, Theor.*

Chim. Acta **79**, 123–140. 87 (1991). The term is also widely used in A. J. Stone, *The Theory of Intermolecular Forces*, (Oxford University Press, Oxford, 2013).

Q17. "yield with" -> "yield"
Corrected.

Q18. *"Detailed analysis of the long-range interactions of the dimers indicates that, for reasonably heavy atoms,..."* – clarify what you mean by "reasonably heavy atoms"
Corrected: (i.e. those atoms being heavier than Ca).

Answers to the corrections and questions made by Prof. A. Shapeev (Skolkovo Institute of Science and Technology)

Q1. *I would suggest to better illustrate some of the aspects of the work. For instance, Chapter 4 talks about a global potential for Yb, quoting the difficulty of merging the atomic (asymptotic expansion at large distances) and molecular (as I understood, direct computation of the interaction). As the interaction energy is a one-dimensional function, I believe this can be nicely illustrated on a graph: I expected to see expansion of the interaction in R-6 and R-8 and graphically see how these functions diverge faster as R decreases than molecular calculations become sufficiently accurate.*
It is not easy to produce a simple self-explanatory plot due to small potential differences that have inverse-power radial dependence. Nevertheless, to answer the question by the Reviewer, the following graph was prepared and will be also presented at the PhD defense.
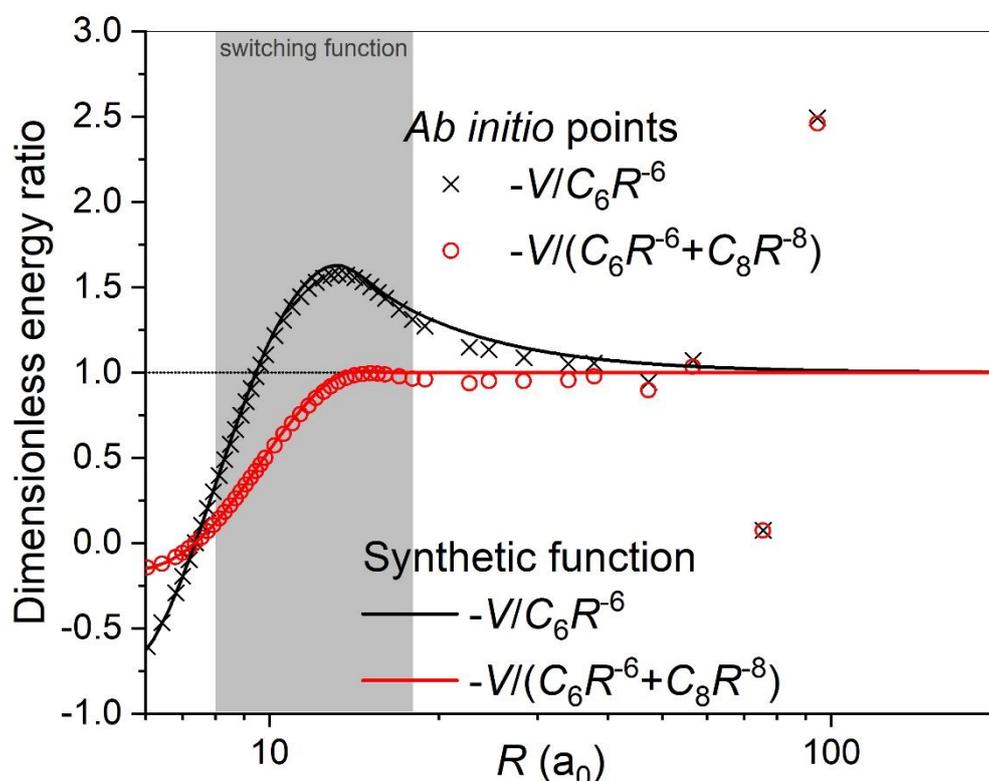
The plots provide the ratio of the *ab initio* points computed for Yb_2 dimer and the related long-range part determined in the atomic calculations and represented either as the sole dipole-dipole dispersion contribution $C_6 R^{-6}$ (black crosses) or as the sum of the dipole-dipole and dipole-quadrupole

dispersion contributions $C_6 R^{-6} + C_8 R^{-8}$ (red circles). Alongside with these plots, the same ratio is provided for the case when the synthetic potential function (eq. (4.1) in the Thesis) is used to match the short- and long-range branches of the global potential. The related curves are provided as solid black and red lines, consistently with the ab initio analogs. The region where the switching function $f(R)$ (eq.(4.2) in the Thesis) is turned on is colored in grey.

In the long-range limit above 25 a_0, *ab initio* points scatter erratically indicating the lack of convergence. At shorter distances, small disagreement of the *ab initio* points and the synthetic function reflects the mismatch in the dispersion contribution accounted for in the molecular calculations and retained in the synthetic function. The curves for the synthetic function converge at very long distance due to the dominant role of the dipole-dipole contribution C_6 to long-range interaction. Deviation at shorter distances illustrates the growing importance of the dipole-quadrupole contribution C_8. The mismatch of the black and red curves (and of the ab initio points as well) is largest in the grey region, where the short- and long-range branches of the potential are joined together and scaled by the switching function $f(R)$. Here, in fact, monomeric and dimeric approaches mix up, leading their strict dualism to break down. As a consequence, the ratios of the global potential and the long-range expansion up to C_8 slightly exceed unity, whereas the plots where the sole C_6 contribution is taken into account attain a maximum peak far above unity.

Moving leftward across the grey region, dimeric calculations become more accurate, while monomeric approaches are no longer adequate for the description of the potential. In fact, the plots start to diverge. The black plots diverge faster than the red ones, as neglecting C_8 in this area is too strong an approximation. Red and black plots cross in a very narrow interval, that corresponds to the validity range of the dimeric approximation for dispersion interaction (analogous to Figure 3.6 in the Thesis). At shorter distances, dispersion interaction plays no longer a significant role.

Q2. Brackets missing in the expression for \hat{H}'(t) after (2.16) and in (2.17)
Corrected.

Q3. Section 2.7.2: is "Effective Core Potential" same as the concept of "Pseudopotentials" as used in the plane-wave basis codes?
Both Pseudopotentials (PPs) used in plane-wave-basis codes and ECPs are based on the following concept: a proper approximate potential can reliably describe the role of innermost orbitals. For this reason, in literature, ECP and PP are often used as synonyms. What actually makes the difference is the method to model this approximate potential. For ECPs, pseudo-orbitals are not generated by means of plane waves, but with levels of theory such as the Multi-Configurational Dirac-Fock method (ECP*n*MDF). This methodological difference led me to use the term "Effective Core Potential" rather than "Pseudopotential".

Q4. Can the defendant explain to a non-specialist in spectroscopy/ultracold physics, what is the practical (scientific) value of the work?
Ultracold measurements can accurately determine the long range coefficients and overall the region of the potential well. The work shows that a scalar-relativistic Coupled Cluster approach adjusted to accurate description of the long-range interaction provides the potential energy curve (PEC) reliable globally. Thus, it can be used as the reference to describe the experimental findings and predict ultracold collisions and spectral properties with the accuracy directly estimated at long range. Vice versa, so obtained potentials can be refined by using the ultracold data.

I would like to thank the members of the PhD jury for their useful notes, corrections and suggestions.

Giorgio Visentin