Calculating lower bound via perturbation theory methods

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Thesis Statements

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Introduction

The main topic of my doctoral work was to calculate lower bound to the electronic energy levels of molecules. The motivation is, that knowing both upper- and lower bounds facilitates bracketing the energy levels. Calculating upper bound is common in quantum chemistry. Expectation value of the Hamiltonian with an approximate wavefunction gives upper bound to the ground state energy. On the other hand, tight enough and easily obtainable approximation is not known in the literature of quantum chemistry.

It is possible to obtain lower bound with an approximate eigenfunction Via Löwdin's bracketing function, reading as:

$$E_L(\varepsilon, \varphi) = \varepsilon + \langle \varphi | (H - \varepsilon)^{-1} | \varphi \rangle^{-1},$$

with φ being a trial function and ε standing for a real number. Provided that ε is an appropriate lower bound to an energy level, $E_L(\varepsilon, \varphi)$ represent a lower bound. Using the bracketing function it is possible to get tight lower bound exhibiting variational property[1]. In spite of that, this method is not practical, as the formula contains the inverse of the Hamiltonian.

The inverse was approximated by polynomial series, generated via partitioning the Hamiltonian as

$$H - \varepsilon = (H^0 - \varepsilon) + V.$$

The series was truncated after the first few term. The approximate formulas must fulfill the following requirements:

- Given an approximate reference function φ, the computational cost of the approximate lower bound should be about the same as the cost of calculating the upper bound $\langle \varphi | H | \varphi \rangle$.

- The approximate lower bound should be at least as tight as the expectation value $\langle \varphi | H | \varphi \rangle$.

- In spite of the approximations, it should be a reliable lower bound.

Thesis statements

Results on Löwdin's bracketing function[2]

1. We proposed to approximate the inverse matrix in the formula of the bracketing function by power series expansion. The expansion is truncated after the first few terms. An arrow shaped zeroth order Hamiltonian was chosen. The working formulae were derived in two different ways: with biorthogonal formalism and based on projector operators.

2. The error of the upper bound calculated as an expectation value of the Hamiltonian depends quadratically on the error of the reference function. We showed that the error of all the approximate lower bound formulae we derived also has a quadratic dependence on the error of the reference function.

3. The working formulae featuring the biorthogonal formalism were implemented in a full configuration interaction (FCI) code, which was already available in our group. Zeroth-, first and second order approximate lower bounds were evaluated at each iteration step of the FCI algorithm. We examined the role of the upper bound substituted into the approximate lower bound formulae. Our analysis revealed, that the behavior of the approximate bracketing function close to the exact energy differs from the exact bracketing function. For this reason a not too tight upper bound should be used.

4. Illustrative calculations on the water and ammonia molecules were presented. We found that the second order approximate lower bound with projection to the Davidson subspace provides a reliable lower bound with essentially no increase in the calculation cost. The lower bound property is violated only at extreme bond lengths in the case of water molecule.

5. To obtain even more reliable lower bound, an improved zeroth order was proposed, termed as thick arrow shaped zeroth order matrix. In this case only the first term of the power series can be evaluated with the same computational effort as the expectation value. The working formulae were also derived both with biorthogonal formalism based on with projector operators.

6. Working formula featuring projector operators were implemented in a FCI code. The effect of choosing the upper bound was investigated for this approximation also. In this case it is rather advantageous to choose tight upper bound. In the thesis only the preliminary numerical results were presented. Results for the water molecule at equilibrium geometry are promising. The lower bound property is violated at extreme bond length, similarly to our previous, cruder approximation.

7. The bracketing function can be interpreted as a second order PT expression with a special choice for the zeroth order resolvent. Reducing this resolvent to the space interacting with the reference via the Hamiltonian, the second order of the so called optimised partitioning is recovered. The latter has been shown to provide the linearised coupled cluster doubles (LCCD) or equivalently, the simplest coupled electron pair approximation (CEPA0) both at the single- and multireference level.

A novel (bi)orthogonalisation procedure[3]

8. In order to calculate the matrix representation of the thick arrow zeroth order Hamiltonian we had to treat an overlapping and redundant basis set. The number of redundant basis vectors (m) is significantly smaller than the number of all basis vectors (N), namely $m \ll N$. We managed to give both orthogonal and biorthogonal vector sets in a way, that all formulae are expressed in closed form and only m dimensional matrix eigenvalue problem or matrix inversion has to be solved.

9. The derived (bi)orthogonalisation procedures were applied in the framework of Bloch-equation based multireference PT.

Publications

[1] Á. Szabados, Zs. Tóth. Löwdin's bracketing function revisited *J. Math. Chem.*, 52:2210, 2014.

[2] Zs. Tóth, Á. Szabados. Energy error bars in direct configuration interaction sequence *J. Chem. Phys*, 143:084112, 2015.

[3] Zs. Tóth, P. R. Nagy, P. Jeszenszki, Á. Szabados. Novel orthogonalization and biorthogonalization algorithms *Theor. Chem. Acc.*, 134:100, 2015.

[4] Zs. Tóth, P. Pulay. Finding symmetry breaking Hartree–Fock solutions: the case of triplet instability *J. Chem. Phys.*, 135:164102, 2016.

Conference talks

- Zs. Tóth and Á. Szabados. *Calculating lower bound to the energy eigenvalues of the Hamiltonian*, Central European Symposium on Theoretical Chemistry(CESTC), Wisła, Poland, 2017

- Zs. Tóth and P. Pulay. *Revisiting Hartree-Fock instability*, Graduate Conference on Theoretical Chemistry(GCTC), Keszthely, Hungary, 2016

Poster presentations

- Zs. Tóth and Á. Szabados. *Calculating lower bound to the energy eigenvalues of the Hamiltonian*, WATOC, München, Germany, 2017

- Zs. Tóth and P. Pulay. *Revisiting Hartree-Fock instability: energy surfaces*, Low-scaling and Unconventional Electronic Structure Techniques Conference (LEUST), Telluride, Colorado (USA), 2016

- Zs. Tóth and Á. Szabados. *Lower bound via Löwdin's bracketing function*, Central European Symposium on Theoretical Chemistry(CESTC), Nagybörzsöny, Hungary, 2014

- Zs. Tóth and Á. Szabados. *Approximate lower bound via Löwdin's bracketing function*, The 8th Congress of the International Society of Theoretical Chemical Physics (ISTCP8) , Budapest, Hungary, 2013