

Chemical bond modelling with correlation effects included.

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Abstract

The one-electron pseudo-atom potential is developed following the chemical bond modelling method proposed earlier by authors [1, 2] in the HF approximation. The exact in the HF approximation bond orbital is the solution of the closed shell HF equation for two electrons in the field of two pseudo-atoms connected with the bond. The closed shell HF bond energy reproduces the bond adiabatic potential fairly well in the vicinity of the equilibrium bond length. However, for larger distances the results are bad due to the deficiency of one closed shell approximation for the bond at large interatomic separation. The few to many configuration calculations of the two-electron problem for the single chemical bond are reported in the present paper. The pseudo-atom potential calculated in the HF approximation at the equilibrium bond length and fixed is used in these calculations. The results for some carbon containing molecules are presented and discussed here.

1 Introduction

This paper is one in a series of papers devoted to the embedding potential problem. The embedding potential enables one to accurately calculate the properties of an important part of a large system, otherwise untractable, by simulating the influence of the environment with an embedding potential. The ultimate goal is to develop the embedding potential which will be equally good for materials with different type of bonding, namely pure ionic, pure covalent, mixed ionic-covalent, and so on. The systems with covalent bonding are the objects of the present paper. Many papers were devoted to this problem especially in the QM/MM method, see [3, 4, 5, 6, 7, 8, 9, 10] and references therein. However, the problem is not completely solved yet and is still actual. Here the simplified particular systems are considered which can be thought of as consisting of two parts connected with a single covalent bond. This problem was addressed earlier by authors [1, 2] in the HF approximation. Special localization procedure was proposed in [1, 2] so that one of non-canonical orbitals of the molecule obtained as a result of this procedure application has properties of the bond orbital and can therefore be considered as an exact (in the HF approximation) bond orbital. The one-electron pseudo-atom potential was developed in [1, 2] to simulate each part of the system so that the exact bond orbital is the solution of the closed shell HF equation for two electrons in the field of both pseudo-atoms. The closed shell HF energy calculated with the help of obtained bond orbital reproduces the adiabatic potential fairly well in the vicinity of the equilibrium bond length. However, for larger distances the results are bad due to the deficiency of one closed shell approximation for the bond at large interatomic separation. In this region the HF two open shells approximation for the bond could be employed instead to give the correct dissociation limit. At the same time, the switching from one two-electron closed shell configuration to two one-electron open shells configuration with increasing the interatomic distance is computationally

inconvenient. Besides, the one configuration approximation itself is not appropriate in the vicinity of the configuration switch and methods beyond the HF approximation must be employed.

The system with two valence electrons is the natural object for calculations beyond the HF approximation and for the first time such calculations were performed by Fock and coauthors in the paper [12] where atom with two valence electrons was considered. The proposed in [12] approach was generalized in the group functions method [13], which can provide grounds for various approximations in the many-electron systems calculations with correlation effects included. The group functions method was indeed applied in [14, 15] to systems consisting of two parts, but without the chemical bond between parts. The two-electron bond is the simplest group function called geminal. A strictly localized geminals method for the description the system with chemical bonds was proposed in [16] and applied to real systems, see [17] and references therein, within the semiempirical approach.

In the present paper the ab-initio methods are employed. The problem of two subsystems connected with a single chemical bond is transformed into the problem of a geminal in the given external potential. The degree of geminal localization is not specified and the external potential is generated as the superposition of two pseudo-atom potentials each simulating one subsystem. The pseudo-atom potentials are generated in the HF approximation, whereas the two-electron problem is calculated with the help of few to many configuration interactions method.

The structure of the paper is as follows: in the section 2 we briefly outline the results obtained in the HF theory. Then in the section 3 the method similar to that developed in [12] is applied to the present problem. Finally, the results of test calculations for some carbon containing molecules are presented and discussed in section 4.

2 Bond orbital equation within HF theory

Consider a molecule consisting of two ion-radicals connected with a single chemical bond within the HF method. Ion-radicals are the closed shells systems. Combining both ion-radicals into the core we arrive at the problem of two bonding electrons outside the closed shells core. If the core is a tightly bounded system so that the state of the core is almost independent on the bond state, the frozen core approximation can be applied and the bond can be considered as a two-electron system in the fixed external potential. The situation is similar to that of the atomic pseudopotential problem, where the core stability is determined by the spatial and energy separation of the core and valence states. However, in the bond problem there is no spatial bond-core separation, and sometimes even the bond-core energy separation is not certain. Therefore the bond-core decomposition of the molecule should be done in a special way to provide a core stability. For this in [1, 2, 11] the energy driven localization was proposed, where the ion-radical orbitals in the molecule were calculated as those non-canonical molecular orbitals which bring the minimum to the ion-radical energy functional. Then the electron density matrix of the molecule can be written as the sum $\rho = \rho_c + \rho_b$ of the core and bond density matrixes. Then the energy of the molecule is $E^{HF}(\rho_c + \rho_b)$ and the following equation can be derived for the bond orbital ϕ_b

$$\left(\widehat{F}(\rho_b) + \widehat{V}^{HF}(\rho_c) - \left\{\widehat{\rho}_c, \widehat{F}(\rho_b) + \widehat{V}^{HF}(\rho_c)\right\}\right) \phi_b = \lambda_b \phi_b \quad (1)$$

where $\widehat{F}(\rho)$ is the Fock operator for closed shell system with the density matrix ρ , the nuclear attraction potential V_{nuc} from all nuclei of the molecule being included, $\widehat{\rho}$ is the density operator, $\widehat{V}^{HF}(\rho)$ is the Coulomb-exchange potential from the closed shell system with density matrix ρ , and the curly brackets denotes the anticommutator.

This equation can be written in a conventional form as

$$\begin{aligned}\widehat{F}_b\phi_b &= \lambda_b\phi_b \\ \widehat{F}_b &= -\frac{1}{2}\Delta + \widehat{V}_{eff} + \widehat{U}_{eff}, \\ \widehat{V}_{eff} &= V_{nuc} + \widehat{V}^{HF}(\rho_c) - \{\widehat{\rho}_c, \widehat{F}(\rho_c)\}, \quad \widehat{U}_{eff} = \widehat{V}^{HF}(\rho_b) - \{\widehat{\rho}_c, \widehat{V}^{HF}(\rho_b)\}\end{aligned}\tag{2}$$

Operator \widehat{V}_{eff} describes the modified interaction of bond electron with the core. Operator \widehat{U}_{eff} describes modified electron-electron interaction of bond electrons. The operator \widehat{U}_{eff} contains the anti-commutator of the core density operator and the Coulomb-exchange potential of the bond. This is not convenient for applications because the inclusion of this term will result in the change of the electron-electron interaction calculations, the most time consuming operation. Therefore as an approximation this term was omitted and \widehat{U}_{eff} was changed for the ordinary Coulomb-exchange potential $\widehat{V}^{HF}(\rho_b)$. In the result of this change the solution of the equation for bond orbital will be no longer orthogonal to the core orbitals. To lessen the bond - core overlap integrals the auxiliary operator $Q\widehat{\rho}_c$ with positive constant Q was added to \widehat{F}_b operator. With large enough Q , the difference between the exact and approximate bond orbitals can be made as small as 0.5% or even smaller.

3 Bond geminal equation

Applying to the system considered the group functions method one can approximately write the total molecule wave-function as the antisymmetrized product of two groups functions

$$\Psi(x_1, x_2, \dots, x_{N_c+2}) = M \widehat{A}[\Psi_c(x_1, \dots, x_{N_c})\Psi_b(x_{N_c+1}, x_{N_c+2})].\tag{3}$$

Here Ψ_c is the N_c -electrons core wave function, Ψ_b is the two-electron geminal, and \widehat{A} is the antisymmetrizer. In this approximation the intra-bond correlations effects are included whereas the bond-core correlations effects are neglected. The core in our case is the comparatively rigid object which can be calculated once, for example at the equilibrium bond length. So the correlations correction to the core energy will be a constant to a good approximation. The influence of the intra-core correlations on the bond-core interaction is also small and we will neglect it. Therefore we arrive at the HF approximation to the core wave function Ψ_c . The core is the closed shells system hence Ψ_c can be written as a single determinant of the core spin-orbitals ϕ_i , $i = 1, \dots, N_c$. In this case one can impose the strong orthogonality condition

$$\int dx \Psi_c^*(x, x_2, \dots, x_{N_c})\Psi_b(x, x_{N_c+2}) = 0,$$

without any loss of generality [12] and this condition tremendously simplified the problem.

According to [12] the equation for geminal in the field of RHF core can be written as

$$\widehat{\mathcal{H}}_b\Psi_b(x_1, x_2) + \sum_{i=1}^{N_c} [\lambda_i(x_1)\phi_i(x_2) - \lambda_i(x_2)\phi_i(x_1)] = E_b\Psi_b(x_1, x_2)$$

and λ_i are Lagrange multipliers to account for the bond geminal - core orbitals orthogonality. Using the explicit equations for λ_i given in [12], the following equation can be derived

$$\widehat{\mathcal{H}}_b = \sum_{i=1}^2 \left(-\frac{1}{2}\Delta_i + V_{nuc}(x_i) \right) + \frac{1}{r_{12}},$$

ϕ_i are functions that define the Ψ_c determinant and λ_i are Lagrange multipliers. There are explicit expressions for λ_i in [12] which lead to the following equation

$$\widehat{\mathcal{H}}_b^{ps} \Psi_b = E_b \Psi_b$$

$$\begin{aligned} \widehat{\mathcal{H}}_b^{ps} = & \widehat{\mathcal{H}}_b + \sum_{i=1}^2 \left[\widehat{V}_c^{HF}(x_i) - \{ \widehat{\rho}_c(x_i), \widehat{F}_c(x_i) \} \right] - \\ & - \left\{ \left[\widehat{\rho}_c(x_1) + \widehat{\rho}_c(x_2) - \sum_{i \neq j}^{N_c} \widehat{\rho}_{\phi_i}(x_1) \widehat{\rho}_{\phi_j}(x_2) \right], \frac{1}{r_{12}} \right\} \end{aligned} \quad (4)$$

where $\widehat{\rho}_\phi$ is the orbital ϕ density operator $|\phi\rangle\langle\phi|$, operator \widehat{V}_c^{HF} is the core HF potential and \widehat{F}_c is the core Fock operator

$$\widehat{V}_c^{HF} = \widehat{J}(\rho_c) - \widehat{K}(\rho_c), \quad \widehat{F}_c^{HF} = -\frac{1}{2}\Delta + V_{nuc} + \widehat{V}_c^{HF}$$

Operator in the equation (4) can be written as a sum

$$\widehat{\mathcal{H}}_b^{ps}(x_1, x_2) = \widehat{\mathcal{H}}_{b1}^{ps}(x_1) + \widehat{\mathcal{H}}_{b1}^{ps}(x_2) + \widehat{\mathcal{H}}_{b2}^{ps}(x_1, x_2)$$

of one-electron

$$\widehat{\mathcal{H}}_{b1}^{ps}(x) = -\frac{1}{2}\Delta + V_{nuc}(x) + \widehat{V}_c^{HF}(x) - \{ \widehat{\rho}_c(x), \widehat{F}_c(x) \}$$

and two-electron

$$\widehat{\mathcal{H}}_{b2}^{ps}(x_1, x_2) = \frac{1}{r_{12}} - \left\{ \left[\widehat{\rho}_c(x_1) + \widehat{\rho}_c(x_2) - \sum_{i \neq j}^{N_c} \widehat{\rho}_{\phi_i}(x_1) \widehat{\rho}_{\phi_j}(x_2) \right], \frac{1}{r_{12}} \right\}$$

operators. Potential in one-electron operator here is exactly the same as \widehat{V}_{eff} in the equation (2) for the bond orbital. The two-electron operator describes the modified electron-electron interaction, the modification being due to the anticommutator. As in the equation (2) for the bond orbital, the modification of electron-electron interaction complicates substantially the calculation procedure. Therefore as an approximation the two-electron operator was changed for the non-modified interaction $1/r_{12}$. At the same time the operator $Q\widehat{\rho}_c$ was added to the one-electron operator, as in the equation for bond orbital, to lessen the influence of the adopted approximation. In result the following equation for the bond geminal was obtained

$$\widehat{\mathcal{H}}_b^{ps} \Psi_b = E_b \Psi_b,$$

$$\widehat{\mathcal{H}}_b^{ps} = \sum_{i=1}^2 \left[-\frac{1}{2}\Delta + V_{nuc}(x_i) + \widehat{V}_c^{HF}(x_i) - \{ \widehat{\rho}_c(x_i), \widehat{F}_c(x_i) \} + Q\widehat{\rho}_c(x_i) \right] + \frac{1}{r_{12}} \quad (5)$$

It is important to note, that the one-electron potential in the equation (5) does not depend on the bond geminal. So this effective potential can be generated within HF method once and employed in the bond geminal calculation with any desirable method (HF, GVB, MCSCF etc.).

4 Results and discussion

In this section the results of the adiabatic potential calculations are presented and discussed. The following molecules were chosen as the test objects: $\text{CH}_3\text{-H}$, $\text{CH}_3\text{-CH}_3$, and $\text{CH}_3\text{-Li}$. The ANO basis was used in calculations, namely 2s1p for H, 3s2p1d for C and Li. Each molecule was calculated twice, first the all-electron calculations of real molecule were performed, and second the two-electron calculations of pseudo-molecule were done with CH_3 and Li in the molecule simulated by one-electron pseudo-atoms C_{ps} and Li_{ps} respectively.

Each molecule (both real and pseudo) was calculated at the following three levels of theory:

1. RHF
2. GVB [18, 19]
3. CASSCF [20]

In each pseudo-molecule there are only two electrons and both are to be correlated so in each level of theory the calculations are straightforward. In these calculations the energy of the bond in the core potential will be obtained. The total energy of the molecule is the sum of bond energy and the core energy. The latter is the closed shells HF core energy calculated with the same density matrix ρ_c as was used in the effective potential \widehat{V}_{eff} calculations. In real molecule the number of electrons is greater than two and to make the comparison with the pseudo-molecule sound the all-electron variant of calculations must be properly chosen. In the present study those all-electron calculations were chosen which correspond to the total molecule wave function in the form (3) with correlated two-electron function Ψ_b and one-determinant core function Ψ_c . In GVB method only one geminal corresponding to the bond was considered. The core orbitals were inactive, though not frozen. In CASSCF two electrons were distributed among 10 orbitals without any restrictions, all other electrons doubly occupy inactive (not frozen) orbitals. Precautions were taken to ensure the iteration process convergence to the proper state. For this the initial approximation was generated in three stages. First, the molecule ground state is calculated within RHF method and canonical MO are obtained. Second, the exact non-canonical MO corresponding to ion-radicals and bond are generated with the help of localization procedure adopted. Third, the calculations are performed to convergence with ion-radicals orbitals frozen. Starting from this initial state the iteration process was found to converge to the correct state for every molecule considered.

In the pseudo-molecule calculations the pseudo-atom potential can be chosen in different ways. It is useless to generate the pseudo-atom potential at each interatomic separation because generation assumed the total molecule calculation in the HF approximation. It is expedient to calculate the pseudo-atom potential at the equilibrium geometry and use this potential for calculation the pseudo-molecule in different geometry. Molecule calculations are performed with the help of AO basis and the problem arises how to transfer the potential from one to another geometry because the potential is non-local and bases in different geometries are different. After several tests we came to conclusion that it is the ion-radical orbitals that must be transferred and not the potential itself. In the procedure adopted the ion-radical orbitals were calculated at the reference geometry. They were reexpanded to the AO basis of the current geometry. Then the core orbitals were obtained as the union of ion-radical orbitals, their possible non-orthogonality being taken into account, and the effective potential \widehat{V}_{eff} from the equation (2) was calculated.

The results of the adiabatic potential calculations for CH_4 molecule are shown at the Figure 1. Parameter Q in the equation (5) was set equal to 100.0 au. One can see from Figure 1 that in the vicinity of the equilibrium bond length the adiabatic potential calculated for pseudo-molecule almost coincides with that for real molecule independently on the calculation method HF, GVB, or CASSCF. It indicates the good quality of the approximate effective potential in the equation (5). For larger bond lengths the adiabatic potential of the pseudo-molecule deviates from that of the real molecule. This deviation increases with the bond length increasing and tends to a constant value 0.15 eV approximately in both GVB and CASSCF methods, the adiabatic potential of the pseudo-molecule being higher than that of real molecule. The reason for this difference is two-fold. First, the fixed pseudo-atom potential approximation was used. Hence the ion-radicals deformation with the molecule geometry change was neglected. Second, due to the incompleteness of AO basis the ion-radical orbitals reexpansion cannot be done exactly and the corresponding error is larger for larger difference in AO positions. Still, the error 0.15 eV at large distances can be considered as acceptable. It is less than the 0.5 eV difference between HF and GVB energies, or 0.4 eV difference between GVB and CASSCF energies at the equilibrium position. Similar results were obtained for two other molecules.

It is an advantage of the effective potential if it is transferable, that is if the potential generated for one molecule could be employed for another molecule calculations. To test the transferability of the pseudo-atom potential, additional calculations of CH₃CH₃ and CH₃Li molecules had been performed with CH₃ and Li pseudo-atom potentials generated with the help of CH₄ and LiH molecules. The calculated adiabatic potentials are presented in Figures 2 and 3 respectively. One can see that here, contrary to the CH₄ case, the adiabatic potentials of pseudo and real molecules differ not only at large bond lengths, but in the vicinity of equilibrium geometry as well, the difference being about 0.3 eV. The reasons of this difference are the same as in CH₄. First is the neglect of ion-radical deformation resulting from its transfer from one molecule into another, and second is the reexpansion error due to the different positions of AO in the reference and current molecules. However, the essential part of the difference between adiabatic potentials for the pseudo and real molecules is the shift along the energy axis by a constant value for all calculation methods. It means that the ion-radical deformation and the reexpansion error is mostly due to the transfer from one molecule to another and less dependent on the bond length. Therefore if the accuracy within 0.3 eV in adiabatic potential is admissible, the same pseudo-atom potential generated for one molecule can be employed for another molecules. If better precision is necessary the correction for the ion-radical deformation should be incorporated. The works on this correction are in progress.

The main advantage of the pseudo-atom potential developed lies in the fact it enables one to reduce the electronic structure calculations of a large molecule with a chemical bond to the calculation of two-electron system in the external potential. The calculations with correlation effects included of the obtained two-electron system is much simpler and less time consuming than similar calculations of the initial molecule.

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References

- [1] Abarenkov, I.V.; Antonova I.M., Int J Quant Chem, accepted for publication
- [2] Abarenkov, I.V.; Smelkov, K.V.; Int J Quant Chem, accepted for publication
- [3] Hernandes, N.; Sanz, J.F. J Comput Chem 1999, 20, 1145
- [4] Reuter, N; Dejaegere, A.; Maigret, B; Karplus, M. J Phys Chem A 2000, 104, 1720
- [5] Singh, U.C.; Kollman, P.A. J Comput Chem 1986, 7, 718
- [6] Antes, I.; Theil, W. J Phys Chem A 1999, 103, 9290
- [7] Das, D.; Eurenus, K.P.; Billings, E.M.; Sherwood, P.; Chatfield, D.C.; Hodoscek, M.; Brooks, B.R. J Chem Phys 2002, 117, 10534
- [8] They, V.; Rinaldy, D.; Rivail, J.-L.; Maigret, B.; Ferenczy, G.G. J Comput Chem 1994, 15, 269
- [9] Gao, J.; Amara, P.; Alhambra, C.; Field, M.J. J Phys Chem A 1998, 102, 4714
- [10] Heully, J.-L.; Poteau, R.; Berasaluce, S.; Alary, F. J Chem Phys 2002, 116, 4829
- [11] Smelkov K.V. "Energy-driven localization and its application to the chemical bond modelling." M.D. Thesis, St. Petersburg State University, 2003. (in Russian)

- [12] Fock, V.A.; Veselov, M.G.; Petrashen, M.I. JETP 1940, 10, 723 (in Russian)
- [13] McWeeny, R. Methods of molecular quantum mechanics; Academic Press: London, 1992.
- [14] Mehías J.A.; Sanz J. F. J. Chem.Phys, 1995, 102, 327
- [15] Mehías J.A.; Sanz J. F. J. Chem.Phys, 1995, 102, 857
- [16] Poirier, R.A.; Surján, P.R. J Comput Chem 1987, 8, 436
- [17] Tokmachev, A.M.; Tchougreeff, A.L. Int J Quant Chem 2002, 88, 403
- [18] Li, J.; McWeeny, R. VB2000 Version 1.6, SciNet Technologies, San Diego, 2002.
- [19] Li, J.; McWeeny, R. Int J Quant Chem 2002, 89, 216
- [20] Anderson, K.; Blomberg, M. R. A.; Fülsher, M. P.; Kellö, V.; Lindh, R.; Malmqvist, P. -Å.; Noga, J.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Siegban, P. E. M.; Urban, M.; Windmark, P. -O. *MOLCAS, Version 2* (University of Lund, Sweden)

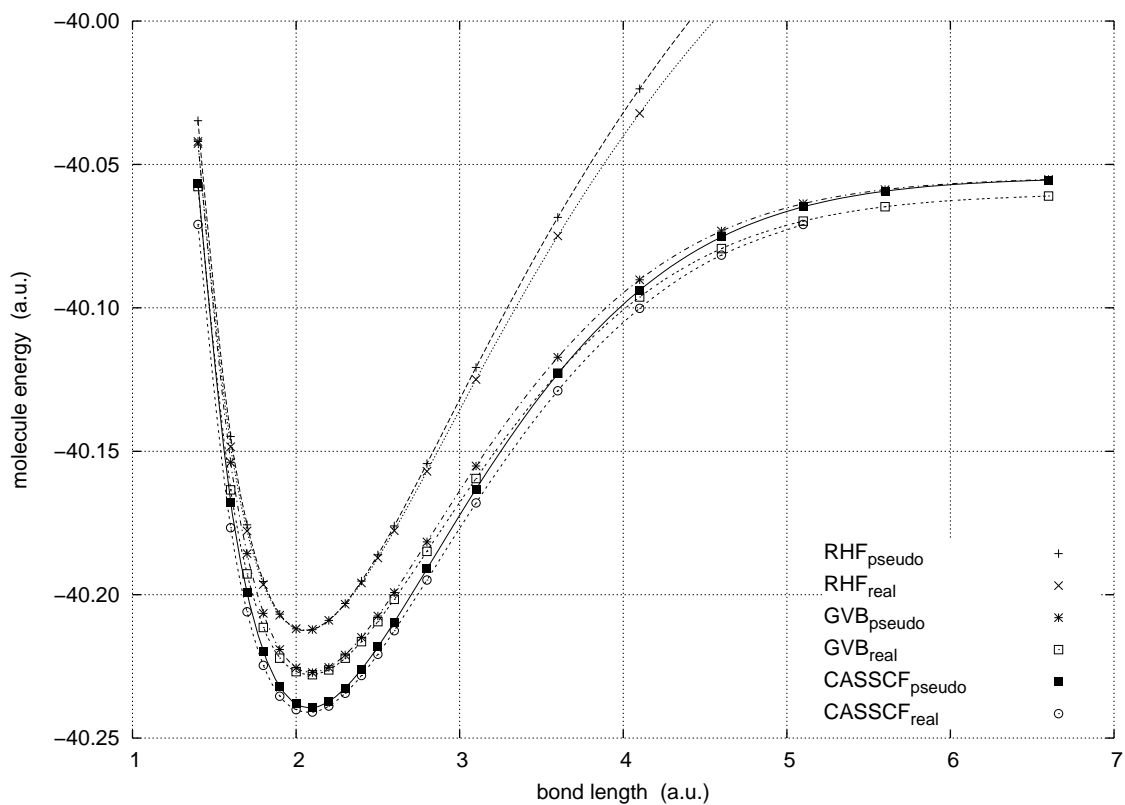


Figure 1: $\text{CH}_3\text{-H}$ and $\text{C}_{ps}\text{-H}$ adiabatic potentials.

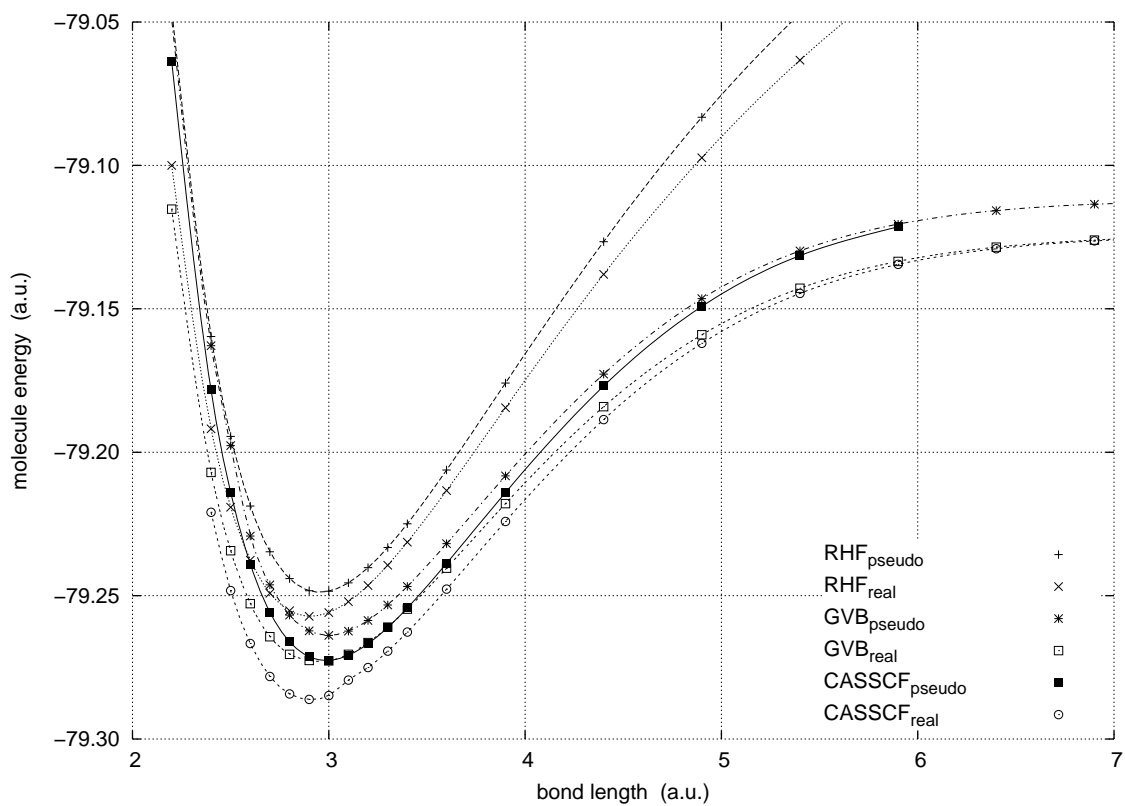


Figure 2: Transferability test. $\text{CH}_3\text{-CH}_3$ and $\text{C}_{ps}\text{-C}_{ps}$ adiabatic potentials.

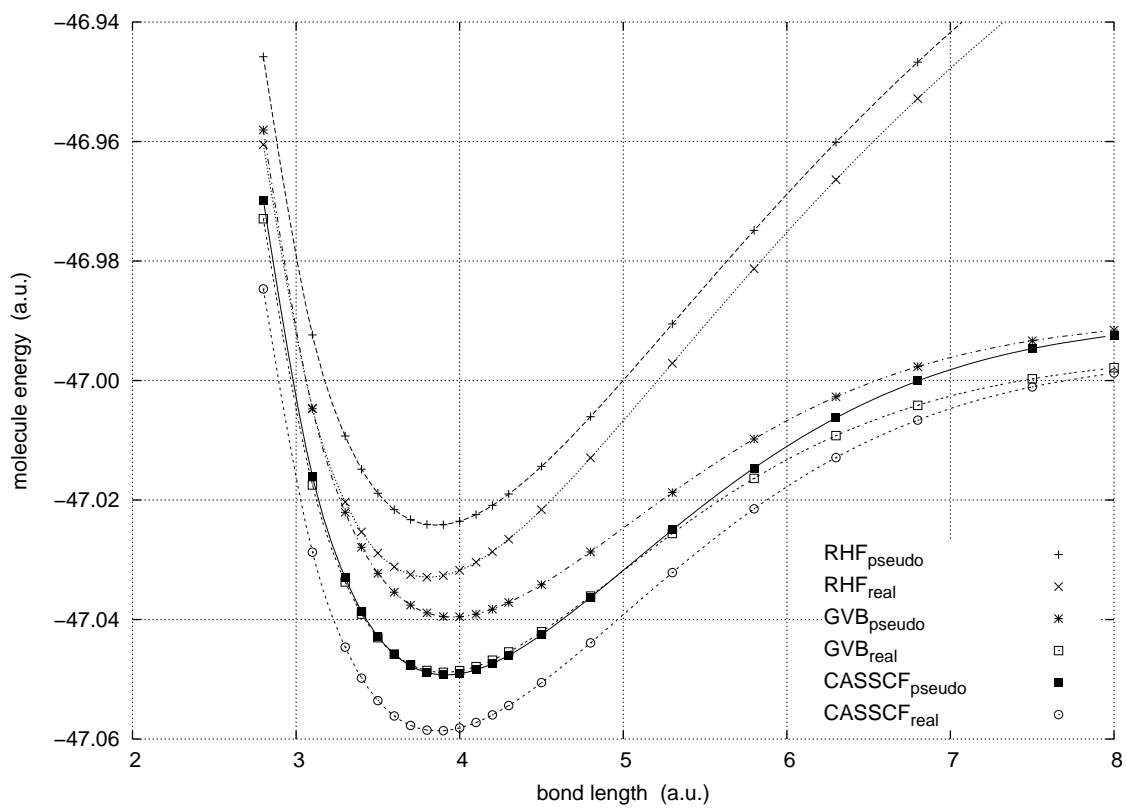


Figure 3: Transferability test. CH₃-Li and C_{ps}-Li_{ps} adiabatic potentials.