

CC-R12, a correlation cusp corrected coupled-cluster method with a pilot application to the Be₂ potential curve

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The concept of wavefunctions with linear r_{12} terms is combined with the coupled-cluster Ansatz at the CCSD and CCSD[T] (formerly CCSD+T(CCSD)) levels. Difficult integrals are avoided by means of completeness insertions in the "standard approximation". A new integral package is used and the "orbital-invariant" formalism is implemented. Applications to the Be atom and the Be₂ molecule on the CCSD and CCSD[T] levels are described. With r_{12} terms the convergence to the basis set limit is much faster than without these.

1. Introduction

A central obstacle on the way to accurate quantum-chemical calculations is the slow convergence of CI-like expansions with extension of the basis. There is no doubt that this slow convergence is due to the inability of traditional quantum-chemical methods to describe the correlation cusp correctly [1–4]. A powerful way to speed up the convergence is the inclusion of terms into the wave-function that depend explicitly on the interelectronic distances r_{ij} , either terms linear in r_{ij} [2,3,5–8] as required by the correlation cusp condition [9] or so-called Gaussian geminals with a Gaussian dependence on r_{ij} [10]. The latter choice has the advantage that no "difficult" integrals need to be evaluated, but the correlation cusp is less well described and there is a need for a sophisticated optimization of non-linear parameters. With linear r_{12} terms difficult integrals arise, in principle, but they can be avoided by careful completeness insertions [3,5], which reduce the computational effort considerably.

So far we have applied the concept of linear r_{ij} terms in Møller–Plesset perturbation calculations

(i.e. many-body perturbation theory with Hartree–Fock as reference) to second and third order [3,5–7] as well as in CID and CEPA calculations [8], getting rather close to the respective basis set limits by actually using only moderate basis sets.

To approach the exact solution of the many-electron Schrödinger equation, one must not only worry about the convergence with increase of the basis size but also about a hierarchy of approximations that – for a fixed basis – eventually leads to full CI. An effective hierarchy in this respect is that of coupled-cluster (CC) methods [11,12].

The most commonly used CC approach, CCSD [13] (including single and double substitutions) is often rather good and certainly superior to Møller–Plesset perturbations theory to second or third order, i.e. MP2 and MP3^{#1}. For higher accuracy inclusion of triple substitution is necessary either in the form of "full" CCSDT [14] or on the simplified level with linearized triples: CCSDT-1 [15]. Usually there is little difference between the results of CCSDT

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^{#1} The names Møller–Plesset theory (MP) or many-body perturbation theory (MBPT) are often used as synonyms. In the Bochum group the notation MP n has been preferred, since this clearly indicates that the zeroth-order reference is Hartree–Fock, while MBPT meant – at least originally – a bare-nuclear Hamiltonian reference. To keep some consistency with the nomenclature of Bartlett for CC methods, we have, in the tables (but not in the text) also adopted his notation for perturbation theory.

and CCSDT-1, and even of the more simplified version CCSD+T(CCSD) in which triple substitutions are treated non-iteratively [16]. In this paper we mainly use CCSD+T(CCSD), and we choose a more compact notation for this, namely CCSD[T]. This notation alludes to the fact that CCSD[T] is related to – but not identical with – another simplification [17] of CCSDT, called CCSD(T), in which triple substitutions are also treated noniteratively.

It appears natural to combine the R12 method with the coupled-cluster approach. We shall present the formulation of this combination (section 2) and illustrate a pilot application. We thought that a “difficult” small molecule should be chosen as test case, namely Be₂. This molecule has been studied by all kinds of theoretical methods including a full-CI calculation [18,19]. We refer to reader to a review of earlier work on Be₂ [20] and some recent papers [18,21,22], as well as to a general discussion of bonding in Be₂ [23]. The binding energy of this molecule is rather small as compared to the absolute errors in conventional calculations. This means that one must be careful that the errors are sufficiently insensitive to changes in the geometry that one does not get spurious interaction effects. With the present method, i.e. CCSD[T]-R12, the absolute errors are reduced so significantly that spurious interactions are unlikely. The results will be discussed in section 3.

2. Theory

We use the second quantization formalism in a particle-hole picture with the Hartree-Fock reference function regarded as the physical vacuum $|0\rangle$. Operators and matrix elements are written in a tensor notation [24,25] (double dots in eq. (1) mark normal products in the particle-hole sense)

$$\tilde{a}_q^p = :a_p^\dagger a_q:, \quad \tilde{a}_{rs}^{pq} = :a_p^\dagger a_q^\dagger a_s a_r:, \quad \text{etc.}, \quad (1)$$

$$h_p^q = \langle p|h|q\rangle, \quad g_{pq}^{rs} = \langle pq|r_{12}^{-1}|rs\rangle, \quad (2)$$

$$\bar{g}_{pq}^{rs} = g_{pq}^{rs} - g_{pq}^{sr}.$$

The Hamiltonian is

$$H_N = F_N + W_N, \quad (3a)$$

$$F_N = \sum_{\kappa,\lambda} f_{\kappa\lambda}^\kappa \tilde{a}_\kappa^\lambda, \quad W_N = \frac{1}{4} \sum_{\kappa,\lambda,\mu,\nu} \bar{g}_{\mu\nu}^{\kappa\lambda} \tilde{a}_{\mu\nu}^{\kappa\lambda}, \quad (3b)$$

$$f_{\kappa}^\kappa = h_{\kappa}^\kappa + \sum_i \bar{g}_{\kappa i}^{\kappa i}. \quad (3c)$$

The spin-orbital basis is assumed orthonormal. We use labels i, j, k, \dots for hole states (spin-orbitals occupied in the reference function), a, b, c for particle states (virtual spin-orbitals) contained in the given basis, while $\alpha, \beta, \gamma, \dots$ mean virtual spin-orbitals that together with i, j, k, \dots form a complete set. Arbitrary spin orbitals of the given basis get the labels p, q, r, \dots and arbitrary spin orbitals of the complete basis $\kappa, \lambda, \mu, \dots$.

In the spirit of coupled cluster (CC) theory we start from an exponential Ansatz for the wavefunction

$$|\Psi\rangle = e^S |0\rangle. \quad (4)$$

The operator S consists of two parts: $S = T + \mathcal{R}$. For $\mathcal{R} = 0$ we have just conventional coupled-cluster theory, while \mathcal{R} takes care of the correct description of the correlation cusp.

$$T = T_1 + T_2 + T_3 + \dots$$

$$= \sum_{i,a} t_i^a \tilde{a}_i^a + \sum_{\substack{i>j \\ a>b}} t_{ij}^{ab} \tilde{a}_{ij}^{ab} + \sum_{\substack{i>j>k \\ a>b>c}} t_{ijk}^{abc} \tilde{a}_{ijk}^{abc} + \dots, \quad (5a)$$

$$\mathcal{R} = \sum_{\substack{i>j \\ k>l}} c_{ij}^{kl} \mathcal{R}_{kl}^{ij}, \quad \mathcal{R}_{kl}^{ij} = \frac{1}{2} \sum_{\alpha>\beta} \bar{R}_{\alpha\beta}^{ij} \tilde{a}_{kl}^{\alpha\beta}, \quad (5b)$$

$$\sum_{\alpha>\beta} \bar{R}_{\alpha\beta}^{ij} \tilde{a}_{kl}^{\alpha\beta} = \sum_{\alpha>\beta} \bar{r}_{\alpha\beta}^{ij} \tilde{a}_{kl}^{\alpha\beta} - \sum_{a>b} \bar{r}_{ab}^{ij} \tilde{a}_{kl}^{ab}, \quad (5c)$$

$$r_{pq}^{rs} = \langle pq|r_{12}|rs\rangle - \langle pq|r_{12}|sr\rangle. \quad (5d)$$

If in (5b) the matrix c_{ij}^{kl} were diagonal, i.e. $c_{ij}^{kl} = \delta_i^k \delta_j^l c_{kl}$, action of \mathcal{R} on $|0\rangle$ would mean that the spin-orbital pair kl is multiplied by $c_{kl} r_{12}$ and then orthogonalized to kl , which leads formally to a sum of doubly excited determinants, involving a complete set (hence the labels α, β). This would correspond to the use of the r_{12} functions taken in previous papers [3,5–8]. The form actually chosen in (5b) means that kl is replaced by ij multiplied by $c_{kl}^i r_{12}$ (and orthogonalized to kl). This is in the spirit of the orbital-invariant r_{12} -approach recently introduced [26] in the context of MP2-R12 theory. With this choice the results do not depend on whether one uses canonical or localized orbitals. Otherwise it would be imperative to use localized ones [7].

With the choice (4) and (5) the intermediate normalization

$$\langle 0 | \Psi \rangle = 1 \quad (6)$$

holds. We follow the traditional way of deriving the CC equations, i.e. we project the Schrödinger equation

$$[(H_N - \Delta E)e^S]_C |0\rangle = 0 \quad (7)$$

from the left onto $\langle 0 | (1 + S^\dagger)$ with a subsequent differentiation with respect to the amplitudes of S^\dagger with the result:

$$\langle 0 | (H_N e^S)_C |0\rangle = \Delta E, \quad (8a)$$

$$\langle 0 | \tilde{a}_{ab}^{\dagger} (H_N e^S)_C |0\rangle = 0, \quad (8b)$$

$$\langle 0 | (\mathcal{R}_{ij}^{\dagger})^\dagger (H_N e^S)_C |0\rangle = 0. \quad (8c)$$

Eqs. (8b) and (8c) determine the amplitudes of operators T and \mathcal{R} . Since the operator \mathcal{R} contains summations over the complete basis, some algebraic manipulations and approximations are needed to evaluate the integrals needed in eq. (8). These include the use of completeness insertions and the neglect of terms that vanish sufficiently rapidly (usually as $(L+1)^{-8}$ or faster) with increasing highest angular quantum number L included in the basis set. Note that all these approximations become exact in the limit of a complete basis, and that the overall convergence with extension of the basis is much faster than in the conventional approach. We follow the same strategy as in our previous work, that leads to the "standard approximation" [3,5]. In this approximation only those \mathcal{R} -containing terms survive in eq. (8), where particle lines of \mathcal{R} are either connected to H_N or to \mathcal{R} , but never open or connected to T . The number of terms that have to be accounted for is then substantially reduced. Eq. (8) will be worked out in detail elsewhere [27]. Here we shall limit ourselves to the working equations. For this purpose let us define the quantities

$$X_{ij}^{rs} = \frac{1}{4} \left((\bar{r}^2)_{ij}^{rs} - \sum_{p>q} \bar{r}_{pq}^{rs} \bar{r}_{ij}^{pq} \right), \quad (9a)$$

$$Y_{ij}^{rs} = X_{ij}^{rs} - \frac{1}{8} (\bar{r}^2)_{ij}^{rs}, \quad (9b)$$

$$V_{ij}^{rs} = \frac{1}{2} \left((\delta_{ir} \delta_{js} - \delta_{jr} \delta_{is}) - \sum_{p>q} \bar{g}_{pq}^{rs} \bar{r}_{ij}^{pq} \right), \quad (9c)$$

$$U_{ij}^{kl} = \frac{1}{4} \left[3(\delta_{ik} \delta_{jl} - \delta_{jk} \delta_{il}) - \sum_{p>q} \bar{r}_{kl}^{pq} \left(\langle pq | \frac{1}{r_{12}} \mathbf{r}_{12} (\nabla_1 - \nabla_2) | ji \rangle - \langle pq | \frac{1}{r_{12}} \mathbf{r}_{12} (\nabla_1 - \nabla_2) | ij \rangle \right) \right], \quad (9d)$$

$$Q_{ij}^{kl} = \sum_{r,m} (X_{ij}^{rl} g_{rm}^{mk} + X_{ij}^{kr} g_{rm}^{ml}), \quad (9e)$$

$$Z_{ijm}^{kln} = \sum_r (Y_{ij}^{rl} g_{rm}^{kn} + Y_{ij}^{kr} g_{rm}^{ln} + Y_{kl}^{rl} g_{rm}^{in} + Y_{kl}^{rn} g_{rm}^{jn}) + \frac{1}{4} \sum_{p,q,r} \bar{r}_{ra}^{kl} g_{pm}^{rn} \bar{r}_{ij}^{pq}, \quad (9f)$$

$$\tilde{B}_{ij}^{kl} = V_{ij}^{kl} - U_{ij}^{kl} - Q_{ij}^{kl} - \sum_m (X_{im}^{kl} f_j^m + X_{mj}^{kl} f_i^m), \quad (9g)$$

$$B_{ij}^{kl}(mn) = \frac{1}{2} (\tilde{B}_{ij}^{kl} + \tilde{B}_{kl}^{ij}) + X_{ij}^{kl} (f_m^n + f_n^m), \quad (9h)$$

$$P_{ij}^{kl} = \frac{1}{2} \sum_{p>q} \bar{r}_{pq}^{kl} V_{ij}^{pq}. \quad (9i)$$

These quantities do not depend on the amplitudes (like t_{ij}^{ab} or c_{kl}^{ij}) in T or \mathcal{R} . We further define intermediates which have to be recalculated for each actual set of amplitudes within the usual iterative procedure for the solution of eq. (8), namely

$$\tau_{ij}^{kl} = t_{ij}^{kl} + t_i^a t_j^b, \quad (10a)$$

$$\tilde{V}_{ij}^{rs} = \sum_{m>n} c_{ij}^{mn} V_{mn}^{rs}, \quad (10b)$$

$$\tilde{X}_{ij}^{rs} = \sum_{m>n} c_{ij}^{mn} X_{mn}^{rs}, \quad (10c)$$

$$O_{ij}^{kl} = \tilde{V}_{ij}^{kl} + \sum_{a>b} \bar{g}_{ab}^{kl} \tau_{ij}^{ab} + \sum_c (\bar{g}_{kl}^c t_i^c + \bar{g}_{kl}^c t_j^c), \quad (10d)$$

$$\tilde{O}_i^k = \sum_j O_{ij}^{kl}.$$

The explicit expressions for the energy and the r_{12} -contributions to the T amplitudes are

$$\begin{aligned} \Delta E &= \Delta E_1 + \Delta E_2, \\ \Delta E_1 &= \sum_{i>j} \sum_{a>b} \bar{g}_{ij}^{ab} \tau_{ab}^{ij}, \\ \Delta E_2 &= \sum_{i>j} \sum_{k>l} c_{ij}^{kl} \tilde{V}_{ij}^{kl}, \end{aligned} \quad (11a)$$

$$D_i^a t_i^a = CC_{\text{conv}}^{(1)} + \sum_k \tilde{V}_{ik}^{ak} - \sum_{k,l} \tilde{V}_{il}^{kl} t_k^a, \quad (11b)$$

$$D_{ij}^{ab} t_{ij}^{ab} = CC_{\text{conv}}^{(2)} + \tilde{V}_{ij}^{ab} - \sum_k (\tilde{V}_{ij}^{kb} t_k^a + \tilde{V}_{ij}^{ak} t_k^b) + \sum_{k,l} \tilde{V}_{ij}^{kl} t_{kl}^{ab} - \sum_{k,l} (\tilde{V}_{il}^{kl} t_{kj}^{ab} + \tilde{V}_{jl}^{kl} t_{ik}^{ab}), \quad (11c)$$

where $D_{ij}^{ab\dots}$ is the usual energy denominator and CC_{conv} stands for the corresponding expressions in conventional coupled-cluster theory. The expression for the r_{12} contribution to the energy is formally the same as in "orbital invariant" MP2-R12 [26]; but differs in the amplitudes of \mathcal{C} . These are obtained from

$$\begin{aligned} \sum_{m>n} B_{kl}^{mn}(ij) c_{ij}^{mn} &= V_{kl}^{ij} - \sum_{m \neq i} \tilde{X}_{mj}^{kl} f_m^i - \sum_{m \neq j} \tilde{X}_{im}^{kl} f_m^j \\ &+ \sum_{c>d} V_{kl}^{cd} t_{ij}^{cd} - \sum_{m>n} c_{ij}^{mn} P_{kl}^{mn} \\ &+ \sum_{m>n,o} (c_{io}^{mn} Z_{mnj}^{klo} + c_{oj}^{mn} Z_{mni}^{klo}) + \sum_c (V_{kl}^{ic} t_j^c + V_{kl}^{cj} t_i^c) \\ &+ \sum_{m>n} (O_{ij}^{mn} + \tilde{g}_{ij}^{mn}) \tilde{X}_{mn}^{kl} - \sum_m (\tilde{O}_i^m \tilde{X}_{mj}^{kl} + \tilde{O}_j^m \tilde{X}_{im}^{kl}). \end{aligned} \quad (12)$$

Denoting the rhs of the last equation as \tilde{c}_{ij}^{kl} the amplitudes of \mathcal{C} are calculated in each iteration as

$$\mathbf{c}_{ij} = \mathbf{B}^{-1}(ij) \tilde{\mathbf{c}}_{ij}, \quad (13)$$

where \mathbf{c}_{ij} ($\tilde{\mathbf{c}}_{ij}$) are columns of the matrix \mathbf{c} ($\tilde{\mathbf{c}}$) for the pair ij . One could, of course, move the ij -dependent terms of $\mathbf{B}(ij)$ to the rhs of eq. (12), avoiding the necessity of solving this equation for each pair separately. However, this has sometimes led to divergencies in practical calculations.

If one treats both W_N and \mathcal{Q}_{ij}^{kl} as perturbations it is quite straightforward to extract the MP4-R12 energies in low order iterations. The order of the amplitudes is now determined as a sum of orders in W_N and in \mathcal{Q}_{ij}^{kl} .

3. Pilot calculations for the Be atom and the Be₂ potential curve

The interaction of two beryllium atoms is a "difficult" problem in quantum chemistry. From several theoretical investigations [18–23, 29] one can conclude that the potential curve is very sensitive to the

level of the theory, as well as to the quality of the basis set. In particular, the large effect of f functions has been stressed [19,28] (e.g. adding a set of f functions can – in conventional CC calculations – change the dissociation energy from 0.7 to 1.86 kcal/mol [28]). It is surprising that such a high level method like CCSDT-1 failed to predict a correct minimum with a 7s3p1d and also with a somewhat larger 7s3p2d basis set [29]. Extending the latter basis by a set of f functions leads to the supposedly correct behaviour [21]. This was a direct challenge for use to compare those calculations with the new CCSD[T]-R12 approach. We have performed calculations of the potential curve with the above mentioned basis sets and with another, fully uncontracted 12s8p4d set [26].

Prior to Be₂, we investigated the Be atom with various basis sets and on various levels of theory. For these atomic calculations we have, in addition, performed calculations with a quite extended fully uncontracted 16s10p6d3f set [8]. The necessary integrals were calculated using the integral package HERMIT [30,31]. The various basis sets, together with the energy components for the Be atom, are described in table 1.

A more elaborate treatment of the Be atom will be published elsewhere [32]. Following a referee's suggestion we make the following comments. With basis A we get the CCD and CCD-R12 values of -91.649 and -92.911 mE_h , respectively (not in table 1). The CCD-R12 result differs from the CCD limit of -92.961 estimated by Salomonson and Öster [33] by 0.05 mE_h . Alexander et al. [34] using the Gaussian geminal method [10,35] estimate -92.95 mE_h , while an older calculated Gaussian geminal result is -92.86 [35] which represents actually the first coupled-cluster calculations with explicit r_{12} dependence. Similarly our CCSD-R12 value (table 1) differs from the estimated limit [33] of 93.667 by 0.06 mE_h . These errors are essentially due to the incompleteness of our basis (the corresponding errors of conventional CCD or CCSD with basis A are ≈ 1.3 mE_h). Our CCSD[T]-R12 result differs from the best estimate of the exact correlation energy of Be of 94.35 mE_h [36] by 0.11 mE_h . We suppose that ≈ 0.06 mE_h are due to basis unsaturation and ≈ 0.05 mE_h to incomplete treatment of triples and neglect of quadruples. The contribution of "singles" ≈ 0.7 mE_h

Table 1

Energy components of the Be atom with various basis sets (in mhartree)

Basis ^{a)}	A	B	C	D	E
SCF	-14573.009	-14572.955	-14572.929	-14572.932	-14572.930
all electrons correlated					
MBPT(2)	-73.454	-70.164	-43.348	-42.529	-41.980
MBPT(2)-R12	-76.021	-75.941	-69.788	-69.699	-69.401
MBPT(4)	-88.729	-86.842	-57.963	-57.963	-57.888
MBPT(4)-R12	-89.873	-89.779	-85.932	-85.948	-85.902
CCSD	-92.345	-90.399	-61.875	-61.801	-61.719
CCSD-R12	-93.606	-93.529	-89.811	-89.806	-89.756
CCSD[T]	-92.985	-91.004	-62.117	-62.045	-61.939
CCSD[T]-R12	-94.241	-94.124	-90.046	-90.042	-89.968
valence electrons correlated					
MBPT(2)	-29.177	-28.018	-28.241	-27.400	-26.876
MBPT(2)-R12	-30.318	-30.256	-29.193	-28.781	-28.388
MBPT(4)	-41.743	-41.688	-41.422	-41.401	-41.359
MBPT(4)-R12	-41.775	-41.730	-41.875	-41.929	-41.930
CCSD	-46.014	-45.881	-45.623	-45.527	-45.470
CCSD-R12	-46.119	-46.107	-46.058	-46.043	-46.011

^{a)} A = [16.10.6.3] from ref. [8], 6 d and 10 f components. B = [12.8.4] from ref. [26], 6 d components. C = [12.5.2.1/7.3.2.1] from ref. [28], 5 d and 7 f components, Gaussian lobes. D = [12.5.2/7.3.2] from ref. [19], 6 d components. E = [12.5.1/7.3.1] from ref. [19], 6 d components.

agrees well with the estimate of Salomonson and Öster [33].

With cusp correction the much smaller basis B gives practically identical results as basis A while without cusp corrections there are significant differences ($\approx 2 \text{ mE}_h$). There is a great jump from basis B to C, D and E (which are all derived from the same 12s5p primitive set [19]). But it is encouraging that even here the r_{12} approach works well, reducing the error from about 30 to 4 mhartree. The deficiency of these three basis sets can be attributed to the lack of functions needed to describe the correlation of the inner shells. For the correlation energy of the valence electrons there are only minor differences between all basis sets.

We have calculated potential curves for Be_2 on the same levels of approximation as for the Be atom (table 1) except for basis A, but we discuss here only the result on CCSD[T] level with and without r_{12} terms. It has been known that without triple excitations the potential curve of Be_2 cannot be described correctly [18]. Moreover there is also evidence from the study of Dierksen et al. [28] at MP4 level that it is important to take care of the corre-

lation of the K shell electrons. We therefore discuss both calculations with full correlation and calculations taking care of the valence-shell correlation only.

Fig. 1 shows fully correlated CCSD[T] curves without correlation cusp corrections for four basis sets (fig. 1a with valence-shell correlation, and fig. 1b with full correlation). With the smallest basis E one finds two minima, an "inner" one near $5 a_0$ and an "outer" one near $8 a_0$, the latter being even the deeper one. Other basis sets lead to qualitatively similar but quantitatively very different curves. With basis C, that is most extended as far as higher angular moments are concerned, a much deeper inner minimum is found and the outer minimum survives only as a shoulder. The importance to include at least one f function in the basis is obvious from fig. 1.

Qualitatively the results with valence-shell or full correlation are similar, but quantitatively there are significant differences. With full correlation all minima are deeper. It is not clear to which extent these differences represent genuine core contributions or just artifacts due the use of a "valence-only" basis.

On fig. 2a and 2b one finds the same potential curves, but now with the correction for the correla-

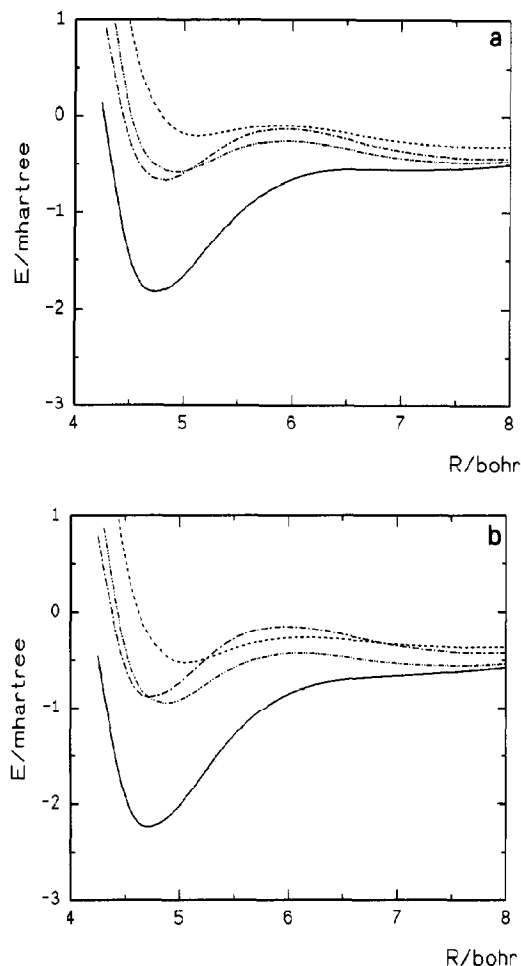


Fig. 1. The CCSD[T] interaction energy curves of Be_2 with various basis sets. For definition of basis sets see table 1. (a) Valence shell correlation and (b) full correlation, (---) B; (—) C; (-·-·-) D; (- - -) E.

tion cusp. Our experience is confirmed that R12 calculations are much less sensitive to details of the basis. The curves for the different basis sets are now much less different. In particular that for basis C differs very little from that without cusp corrections (the total energies differ, of course, by a constant shift since the individual Be atoms are better described with cusp correction). Even basis B which does not contain an f function leads to a reasonable binding energy at the inner minimum. There were some numerical-stability problems that did not allow us to evaluate this curve beyond $\approx 5.5 a_0$.

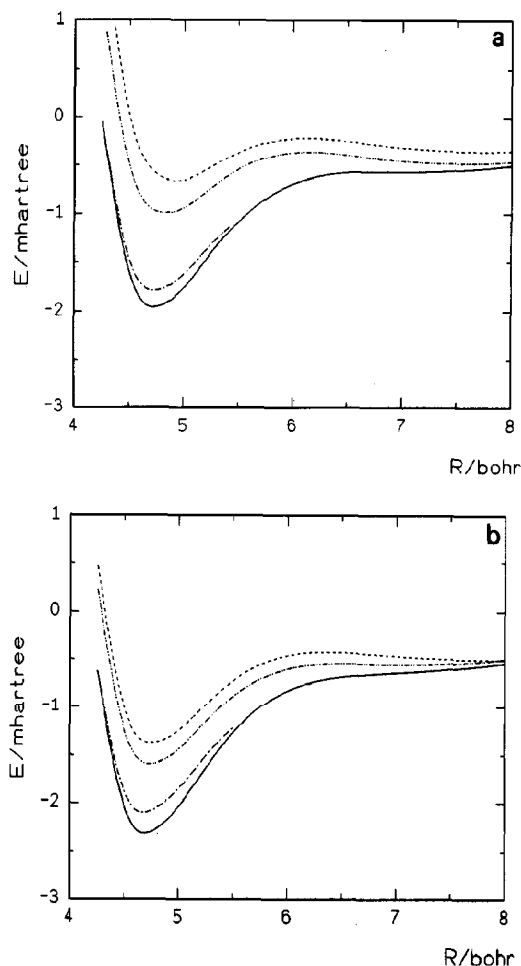


Fig. 2. The CCSD[T]-R12 interaction energy curves of Be_2 with various basis sets. For definition of basis sets see table 1. (a) Valence shell correlation and (b) full correlation, (---) B; (—) C; (-·-·-) D; (- - -) E.

Again there are significant differences between the curves for valence-shell correlation only and for full correlation. For the latter case there is less difference between the different basis sets. Artifacts due to the use of a "valence-only" basis are less likely now, since there is much less error in the K-shell correlation energy.

Some more detailed information on the various potential curves near the (inner) minimum is found in table 2, where in addition the results of MP4 calculations as well as of calculations with only the valence-shell correlation are displayed.

Table 2

Interaction energies of Be₂ at selected interatomic distances near the equilibrium geometry (in mhartree)^{a)}

Basis set ^{b)} R (a ₀)	B	C	D	E
all electrons correlated				
MBPT(4)-R12				
4.50	-	-2.786 (-0.298)	-2.253 (-1.071)	-2.186 (-1.897)
4.75	-	-3.245 (-0.220)	-2.754 (-0.863)	-2.661 (-1.363)
5.00	-	-3.117 (-0.150)	-2.689 (-0.689)	-2.577 (-0.967)
CCSD[T]-R12				
4.50	-1.883 (-1.302)	-2.044 (-0.120)	-1.243 (-0.865)	-1.015 (-1.573)
4.75	-2.079 (-1.197)	-2.296 (-0.066)	-1.588 (-0.678)	-1.376 (-1.077)
5.00	-1.852 (-1.115)	-2.037 (-0.022)	-1.442 (-0.527)	-1.247 (-0.727)
valence electrons correlated				
MBPT(4)-R12				
4.50	-2.431 (-1.316)	-2.277 (-0.200)	-1.426 (-0.640)	-0.985 (-1.057)
4.75	-2.943 (-1.233)	-2.838 (-0.168)	-2.069 (-0.517)	-1.737 (-0.765)
5.00	-2.890 (-1.146)	-2.789 (-0.136)	-2.117 (-0.409)	-1.865 (-0.544)
CCSD[T]-R12				
4.50	-1.458 (-1.226)	-1.592 (-0.150)	-0.486 (-0.577)	+0.037 (-0.959)
4.75	-1.788 (-1.129)	-1.947 (-0.126)	-0.977 (-0.461)	-0.590 (-0.680)
5.00	-1.627 (-1.027)	-1.763 (-0.103)	-0.941 (-0.361)	-0.654 (-0.475)

^{a)} Correlation cusp corrections are given in parentheses.^{b)} For definition of basis sets see table 1.

One of the essential messages is that inclusion of r_{12} terms speeds up the convergence to the basis set limit. It is also important to include the correlation energy of the core, but this is relatively cheap in the R12 approach. In the conventional approach reliable calculations including the K shell require that the basis contains steep polarization functions. Otherwise spurious effects are likely. This is not necessary in the presence of r_{12} terms. One can not dismiss with triple excitations. In their absence even CCSD-R12 calculations do not find the inner minimum.

It should be mentioned that basis set superposition errors, which only matter at the microhartree level for conventional calculations for the basis sets used here [28] are entirely negligible in the calculations with r_{12} terms.

We are now on much safer grounds for an extrapolation to the "exact" Be₂ curve. We are confident that we have reached the basis set limits on all levels of approximation, but not the limit of the hierarchy that leads to full CI. From previous results we can conclude that inclusion of complete triple [18] and approximate quadruple excitations [37] should

lower the minimum by nearly one mE_h. Calculations on this level are planned.

From previous experience at the MP2 level one should expect good agreement between our calculations and the results of the CBS ("complete basis set") extrapolation of Peterson et al. [38,39]. In the present case CBS extrapolations for QCISD(T) and CCSDT are available [22]. These are significantly lower, i.e. closer to experiment, than our CCSD[T] results and also quite different from one another. It would be premature to comment on these differences.

That triple and quadruple excitations are so important for Be₂ is, of course, an indication that Be₂ represents a case where a correlation treatment should be based on an MC-SCF reference function, namely with an active space consisting of $2\sigma_g$, $2\sigma_u$, $3\sigma_g$, $3\sigma_u$. The occupation numbers of these orbitals are roughly 1.9, 1.9, 0.1, 0.1, respectively at infinite nuclear separation and 1.95, 1.785, 0.25, 0.03 at $R=5$ a₀ [40]. The occupation numbers of $3\sigma_g$ and $3\sigma_u$ are too large to treat these MOs as virtual.

The present calculations on Be₂ are the first where the absolute error of the curves (which is of the or-

der of a few millihartree) is not large compared to the quantity to be calculated, namely the binding energy.

4. Conclusions

It has been possible to combine the R12 approach with the coupled-cluster methods on the CCSD[T] level (former terminology CCSD+T(CCSD)). Although a substantial programming labour was necessary, the computations for CCSD[T]-R12 are hardly more expensive than for CCSD[T] without R12, at least with the new integral program [30]. In the MP-context where the evaluation of the integrals is the dominating step, the switch from MP2 to MP2-R12 for the same basis required about 4 times more computer time. On the CCSD[T] level the integral evaluation only costs a minor fraction of the overall time and the cost for the extra terms by which CC-R12 differs from CC is almost negligible.

The superiority of the CC-R12 results over those from conventional CC (on all excitation levels) is obvious from the present study, even if Be₂ may not have been the most convenient test case, since here the convergence of the CC excitation level to full CI is at least as crucial as the convergence with the size of the basis.

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