

Combining long-range configuration interaction with short-range density functionals

Thierry Leininger^{a,1}, Hermann Stoll^a, Hans-Joachim Werner^a, Andreas Savin^b

^a *Institut für Theoretische Chemie, Universität Stuttgart, D-70550 Stuttgart, Germany*

^b *Laboratoire de Chimie Théorique, Université Pierre et Marie Curie, F-75252 Paris, France*

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Abstract

A density functional for short-range electron–electron interaction recently developed by one of us, has been implemented into a multi-reference configuration-interaction code with explicit treatment of long-range interaction only. Possible advantages of such an approach are discussed, using as examples some closed-shell atoms (Be, Ne) and diatomics (H₂, Li₂, C₂, N₂, F₂). © 1997 Published by Elsevier Science B.V.

1. Introduction

The two-particle electron–electron interaction, $1/r_{ij}$, with its singularity for $r_{ij} \rightarrow 0$, is the main source of the complexity of molecular wavefunctions ψ : long configuration-interaction (CI) expansions in terms of extended one-particle basis sets are necessary to properly describe the correlation cusp of ψ at $r_{ij} \rightarrow 0$ [1]. One possibility to overcome this difficulty is the explicit introduction of the inter-electronic coordinates r_{ij} into ψ ; while being computationally demanding, this leads to highly accurate wavefunctions [2,3]. As an alternative, one may modify the Hamiltonian in such a way that the correlation cusp of ψ disappears; this can be done, e.g., by replacing $1/r_{ij}$ with $g(r_{ij})/r_{ij}$ where $g(r_{ij})$ is a suitable cut-off function for $r_{ij} \rightarrow 0$. This

amounts to retaining only the long-range part of the electron–electron interaction, and thus is just the opposite to what has recently been proposed by Gill et al. [4]. Of course, the short-range part of $1/r_{ij}$ cannot simply be neglected, without changing the spectrum of the Hamiltonian significantly. However, an efficient and accurate means of implicitly treating $[1 - g(r_{ij})]/r_{ij}$, without ever taking explicit care of the correlation cusp, is at hand via density-functional theory (DFT) (cf. e.g. [5]). Current density functionals are known to yield good approximations for molecular many-body effects, within a formal one-particle picture. They should perform even better when applied to a description of the short-range (dynamical) correlation hole only, with long-range correlation and quasi-degeneracy effects explicitly treated by a CI-like scheme.

The idea of combining the advantages of CI and DFT approaches has quite a long history, cf. e.g. [6]. The particular way of combination sketched above

¹ Present address: Max-Planck-Institut für Physik komplexer Systeme, D-01187 Dresden, Germany.

was originally suggested some time ago [7], but only recently have parametrizations of short-range density functionals become available [8–10], so that application to molecules is within reach now. Such applications are presented in Section 3, after a brief outline of the basic formulae and of the implementation of the method in Section 2.

2. Theory

Let

$$\mathcal{H} = \sum_i h(i) + \sum_{i < j} \frac{1}{r_{ij}} \quad (1)$$

be the molecular Hamiltonian, with h representing its one-electron part. Consider now a separation of the electron–electron interaction into a long-range and a short-range part:

$$\frac{1}{r_{ij}} = \frac{g(r_{ij})}{r_{ij}} + \frac{1 - g(r_{ij})}{r_{ij}}. \quad (2)$$

A convenient choice of $g(r_{ij})$, both from a physical and a computational point of view, is

$$g(r_{ij}) = \text{erf}(\mu r_{ij}), \quad (3)$$

where $\text{erf}(x)$ is the standard error function. With this choice, the first term in (2) quadratically approaches $2\mu/\sqrt{\pi}$ as $r_{ij} \rightarrow 0$, while the second term exponentially approaches zero as $r_{ij} \rightarrow \infty$. It is easy to see that energy minimization of the expectation value of the Hamiltonian of Eq. (1) is equivalent to that of

$$\mathcal{H}^{\text{lr}} + E^{\text{sr}}[\rho], \quad (4)$$

with

$$\mathcal{H}^{\text{lr}} = \sum_i h(i) + \sum_{i < j} \frac{g(r_{ij})}{r_{ij}}, \quad (5)$$

and

$$E^{\text{sr}}[\rho] = \min_{\psi_\rho} \langle \psi_\rho | \sum_i h(i) + \sum_{i < j} \frac{1}{r_{ij}} | \psi_\rho \rangle - \min_{\psi_\rho} \langle \psi_\rho | \mathcal{H}^{\text{lr}} | \psi_\rho \rangle. \quad (6)$$

Here, the long-range Hamiltonian \mathcal{H}^{lr} is supplemented by an energy functional depending on the

one-particle electron density ρ . In the definition of $E^{\text{sr}}[\rho]$, ψ_ρ denotes the set of all (antisymmetric) wavefunctions yielding a given ρ .

The first term in (6) is just the definition of the usual Kohn–Sham density functional [11], while the second one only differs in that the electron–electron interaction is restricted to its long-range part. Thus, when taking the difference, we are left, in the simplest (local density) approximation (xc -LDA), with the terms

$$E^{\text{sr}}[\rho] = U_c^{\text{sr}}[\rho] + \int \rho \epsilon_{xc}^{\text{sr}}(\rho) d\mathbf{r}, \quad (7)$$

where

$$U_c^{\text{sr}}[\rho] = \int \rho(\mathbf{r}_1) \frac{1 - g(r_{12})}{r_{12}} \rho(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (8)$$

is the short-range Coulomb interaction, and $\epsilon_{xc}^{\text{sr}}(\rho)$ is the exchange–correlation energy per particle of a homogeneous electron gas with (modified) electron–electron interaction $[1 - g(r_{12})]/r_{12}$. An expression for the exchange part of $\epsilon_{xc}^{\text{sr}}$ can be found in Ref. [10]; numerical data for the correlation part, restricted to the non-spin-polarized case, have also been derived in [10], and an analytical parametrization for ϵ_c^{sr} is available from the present authors.

As an alternative (denoted c -LDA in the following), one can invoke the LDA approximation for correlation only, while evaluating short-range exchange exactly, using its Hartree–Fock (HF) expression involving the (full) one-particle density matrix.

The separation between \mathcal{H}^{lr} and $E^{\text{sr}}[\rho]$ is controlled by the parameter μ in Eq. (3); an optimum between economy and accuracy should be reached for finite μ values intermediate between the Kohn–Sham (KS) limit ($\mu = 0$) and the CI limit ($\mu \rightarrow \infty$). Of course, this optimum is related to a characteristic length of the system under consideration, and hence is expected to be different for atomic shells with different main quantum numbers. Application of the method in a pseudopotential context, with explicit treatment of the valence-electron system only, seems therefore to be most rewarding. The method has been implemented into the ab initio program system Molpro [12]. A simple modification of the integral code Seward [13] is sufficient to generate the two-electron integrals $\langle pq|rs \rangle$ with long-range interaction: the

sum of the exponents of the four Gaussians involved, $\eta_p + \eta_q + \eta_r + \eta_s$, has to be supplemented by $(\eta_p + \eta_q)(\eta_r + \eta_s)/\mu^2$. The short-range Coulomb interaction $U_c^{sr}[\rho]$, as well as the corresponding non-local exchange, are calculated directly from the sets of unmodified and modified integrals, while the LDA expressions for $\epsilon_x^{sr}(\rho)$, $\epsilon_c^{sr}(\rho)$ are evaluated over a grid, using the Molpro DFT implementation [14]. These quantities are used to modify in an appropriate way, cf. Eqs. (4) and (7), the energy expression of the multi-reference CI (MRCI) code [15–17], for calculations involving long-range integrals only; in addition, the corresponding functional derivatives, determined analogously, are inserted as potentials in the CI iteration. Since input and output densities ρ (and density matrices) are different, in general, we repeat the MRCI with updated short-range quantities until self-consistency is reached. Note that although completely general wavefunctions are admitted, within the MRCI, the method is restricted, at its present stage, to wavefunctions dominated by a closed-shell reference due to the use of non-spin-polarized short-range density functionals (cf. above).

3. Results

3.1. Atoms

Since preliminary results for two-electron atoms have been published in Ref. [10], we concentrate on first-row atoms and choose Be and Ne as examples of atoms with preponderance of static/dynamic correlation effects.

For Be (cf. Fig. 1), we performed single-reference averaged-coupled-pair-functional (ACPF) [18] calculations, using the (uncontracted) *spdf* part of Dunning's *v5z* basis set [19] and including up to double excitations from both *K* and *L* shells. At $\mu \rightarrow \infty$, i.e. in the limit of a conventional ACPF calculation, the difference to the 'experimental' non-relativistic energy [20] is ~ 0.1 eV. The deviations at the other end, $\mu = 0$, i.e. for conventional Kohn-Sham (KS) calculations, are much larger 6.0 and -3.6 eV for *xc*-LDA and *c*-LDA, respectively. With increasing μ , these deviations rapidly and monotonically decrease to ~ 0.1 eV at μ -values in the range between 3 and 4, with a slightly better convergence for the *xc*-

LDA–CI coupling than for the *c*-LDA–CI one. Note that pure long-range ACPF (with HF-like short-range exchange – label 'HF' in Fig. 1) yields deviations of between 0.8 and 1.0 eV in this μ -interval, indicating the validity and efficiency of LDA for describing short-range correlation effects. It is seen from the μ -dependence of the curves in Fig. 1 that there is a change in the slope around $\mu = 1$; this change is related to the difference in the characteristic inter-electronic length of the $1s^2$ and $2s^2$ shells, the former controlling the behaviour for large μ . It is to be expected, therefore, that the convergence with μ is much improved for valence-shell effects alone. In fact, when subtracting Be and Be^{2+} energies, deviations < 0.1 eV are already reached for μ -values in the range 0.5...1.0. Note that these values (in bohr^{-1}) correspond to 'break-even' points between short- and long-range interaction at inter-electronic distances of 0.3...0.5 Å – for comparison, the valence-shell radius of Be is ~ 1.1 Å [21].

For Ne, let us concentrate on valence-shell effects from the outset (cf. Fig. 2), by using energy-consistent pseudopotentials replacing the K shell [22], together with an extended (uncontracted) 9s9p4d3f2g valence basis set [22] (*v5z* polarization functions from [26]); correlation effects are treated at the single-reference ACPF level again. The deviation from the estimated limit (determined from large-basis-set pseudopotential CCSD(T) calculations, corrected for the difference between experimental [20] and calculated all-electron correlation energy) is quite substantial here (0.6 eV); $\sim 25\%$ of the error is due to the neglect of triples with ACPF, most of the rest has to be attributed to the absence of *h* and higher polarization functions. In the following, we restrict the discussion of the DFT-CI coupled results to deviations from the ACPF limit at $\mu \rightarrow \infty$. The best results are obtained with *c*-LDA: here, a rapid and (nearly) monotonic convergence is observed, with a reduction of the $\mu = 0$ KS error (with respect to the CI limit) of 6.5 eV to ≤ 0.7 eV for $\mu \geq 1$. The maximum *xc*-LDA error for $\mu \geq 1$ is around 1.3 eV, but still this is only $\sim 0.14\%$ of the total valence energy and is of the same order of magnitude (and the same sign) as the ACPF error itself. It is interesting to see, from the HF curve, that only $\sim 10\%$ of the (dynamical) correlation effects in Ne are treated explicitly, i.e. by long-range ACPF, for $\mu = 1$; again, this

underlines the significant improvement induced by the short-range density functionals. As already mentioned, an important advantage of the present DFT-CI coupling should be the reduced one-particle/many-particle basis-set requirements. In fact, the computational efficiency of pure KS calculations (i.e. no need for d, f polarization functions or configurational mixing at $\mu = 0$) partially transfers to intermediate μ -values: for $\mu = 1$, restriction to a s, p basis

set yields an energy loss of 0.5 eV for c -LDA, the restriction to a single determinant another 0.3 eV; the corresponding numbers in the ACPF limit ($\mu \rightarrow \infty$) are 4.0 eV each.

3.2. Molecules

Let us begin with the simplest case here – H_2 . CISD calculations have been performed here, using

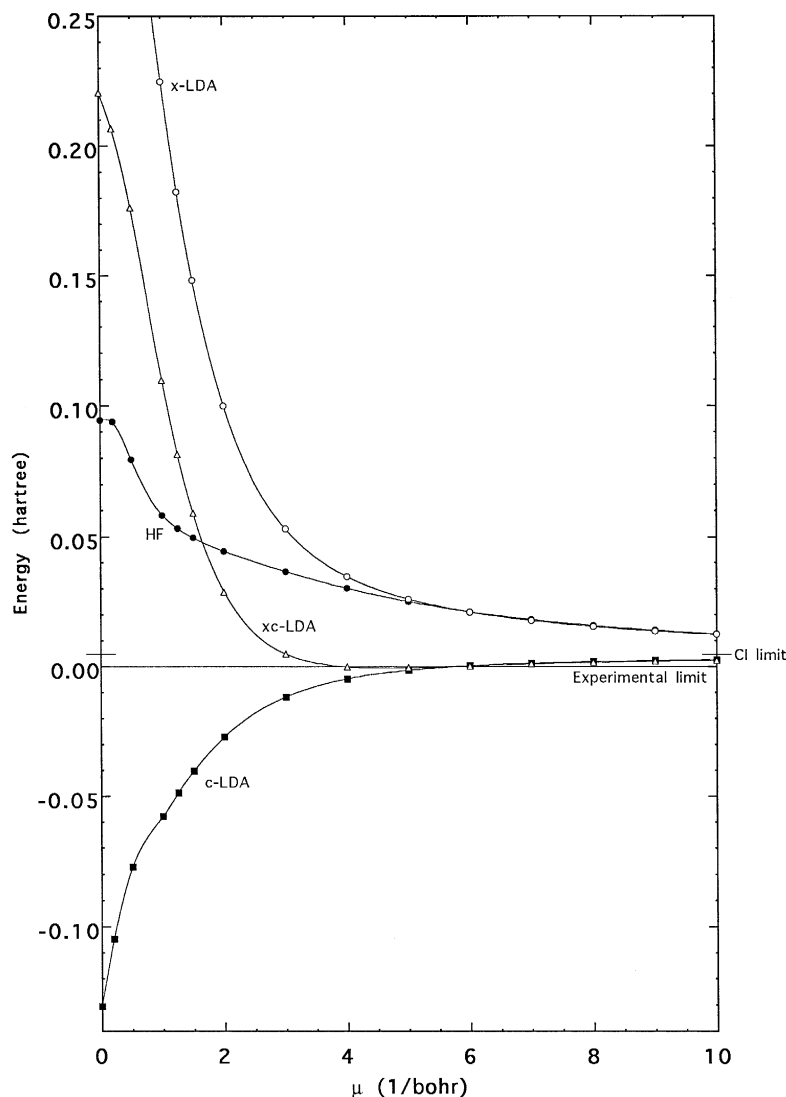


Fig. 1. Total energy of the Be atom, relative to the (non-relativistic) experimental limit [20], for various short-range methods coupled to long-range ACPF.

the *spdf* part of Dunning's *v5z* basis set [19], and results have been obtained, for each μ -value separately, for the bond length r_e , vibrational frequency ω_e , and dissociation energy D_e . The D_e values, cf. Fig. 3, are taken with respect to the (conventional) SCF energies of the separate atoms. It is seen that the convergence to the CI limit is quite rapid for D_e : *xc*-LDA is too small by 1.0 eV, *c*-LDA too large by 1.5 eV for $\mu = 0$, but a uniform accuracy of better

than 0.05 eV is reached for $\mu \geq 1$. The improvement with DFT-CI mixing is less spectacular for r_e , because the KS results at $\mu = 0$ are already quite accurate (to 2 pm), but here too the improvement is notable (deviation from the CI limit < 0.2 pm for $\mu \geq 2$). For ω_e KS errors of ± 300 cm^{-1} at $\mu = 0$ become < 20 cm^{-1} (0.5%) for $\mu \geq 2$. In all cases, pure long-range CI (HF curve in Fig. 3) is much inferior to the DFT-CI results, by ~ 0.8 eV for D_e at

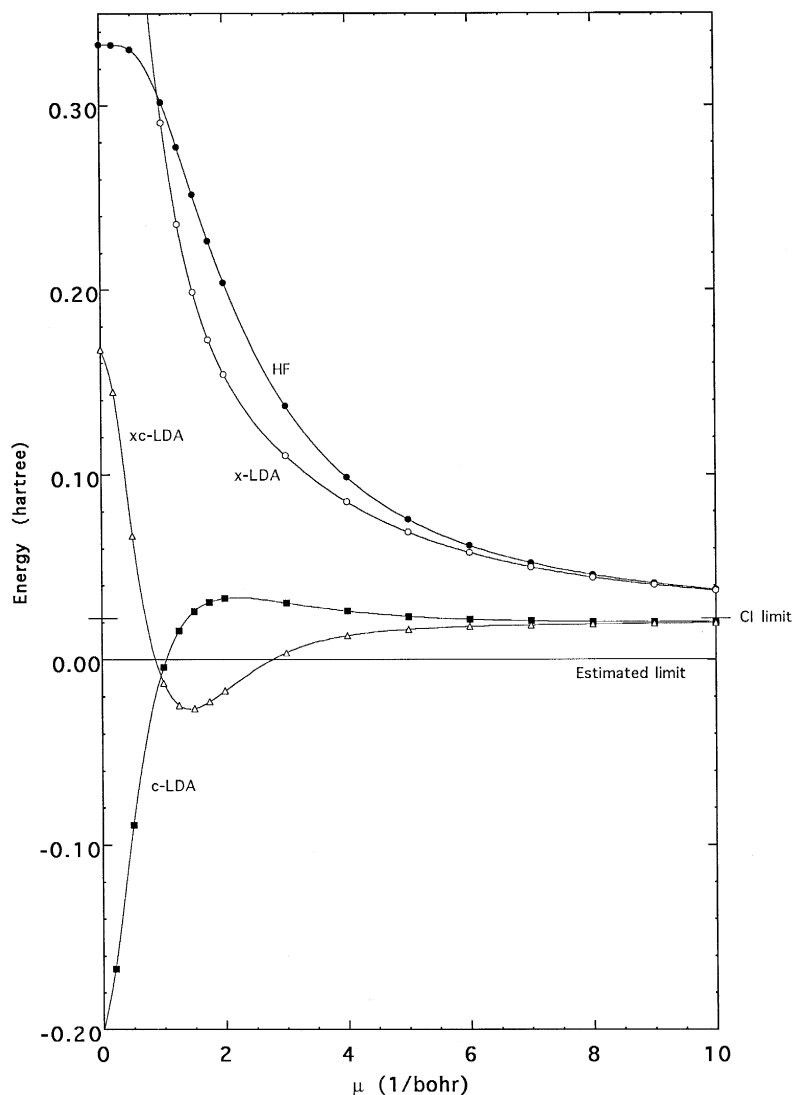


Fig. 2. Valence energy of the Ne atom, relative to a combined theoretical/experimental limit, cf. text, for various short-range methods coupled to long-range ACPF.

$\mu = 1$, and 100 cm^{-1} for ω_e at $\mu = 2$ — this is further indication of the physical soundness of the DFT approximation for describing short-range dynamical correlation. It is interesting to note that even in the $r \rightarrow \infty$ limit of the H_2 curve, the present DFT-CI coupling scheme seems to work moderately well, although the use of non-spin-polarized density functionals is certainly not optimum: while at $\mu = 0$, xc -LDA and c -LDA are off by 0.11 and 0.21 E^h , respectively, the deviations from the exact result

(-1 E^h) , are only 6 mE^h at $\mu = 2$. Turning now to the question of the computational efficiency of the DFT-CI coupling for H_2 , we find that reasonable results can be obtained already at the s -limit, i.e. with a basis set containing s functions exclusively. At the xc -LDA KS limit ($\mu = 0$), this leads to quite small errors, with respect to the extended $spdf$ basis set mentioned above, of 0.1 pm for r_e , 39 cm^{-1} for ω_e , and 0.1 eV for D_e ; at the μ -values discussed above ($\mu = 1$ for D_e , $\mu = 2$ for r_e and ω_e), the

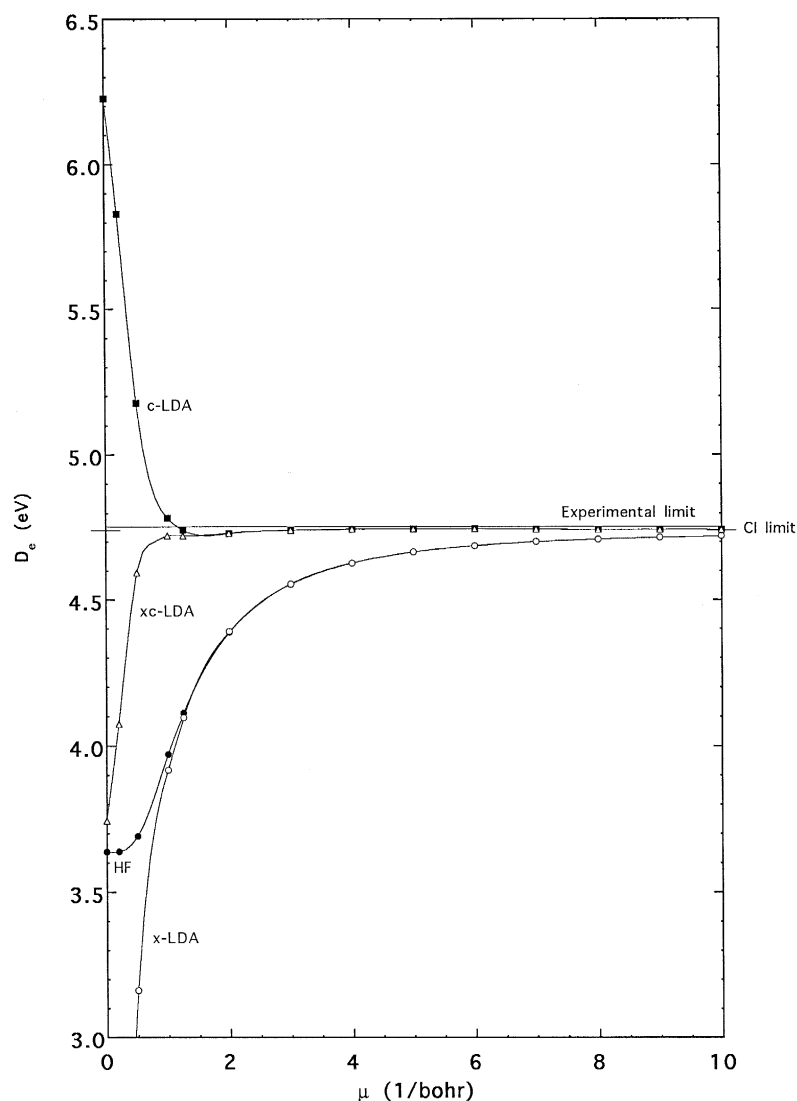


Fig. 3. Dissociation energy D_e of H_2 , relative to the $E^{\mu \rightarrow \infty}$ ($r \rightarrow \infty$) limit, for various short-range methods coupled to long-range CISD.

errors are still tolerable (< 0.1 pm for r_e , 66 cm^{-1} for ω_e , 0.2 eV for D_e), while they blow up, of course, at the CI limit ($\mu \rightarrow \infty$): $\Delta r_e = 0.5$ pm, $\Delta \omega_e = 130$ cm^{-1} , $\Delta D_e = 0.5$ eV.

Li_2 is a case with strong near-degeneracy effects and a quite unusual bond-length shortening, by 10 pm, due to correlation. We performed CISD calculations for Li_2 , using our energy-consistent pseudopotentials [23], together with a flexible even-tempered

$8s6p2d$ valence basis set. The results at $\mu \rightarrow \infty$ ($r_e = 2.68$ Å, $D_e = 1.04$ eV, $\omega_e = 346$ cm^{-1}) are quite near to the experimental values ($r_e = 2.67$ Å, $D_e = 1.06$ eV, $\omega_e = 351$ cm^{-1}). Results for r_e at intermediate μ values are shown in Fig. 4; it is seen that deviations from the CI limit at $\mu = 0$ ($\Delta r_e = 3$ pm for c -LDA, 10 pm for xc -LDA, at $\mu = 0$) have already damped out to < 1 pm for $\mu = 1$; for ω_e (not shown) changes are $< 0.5\%$ in the interval

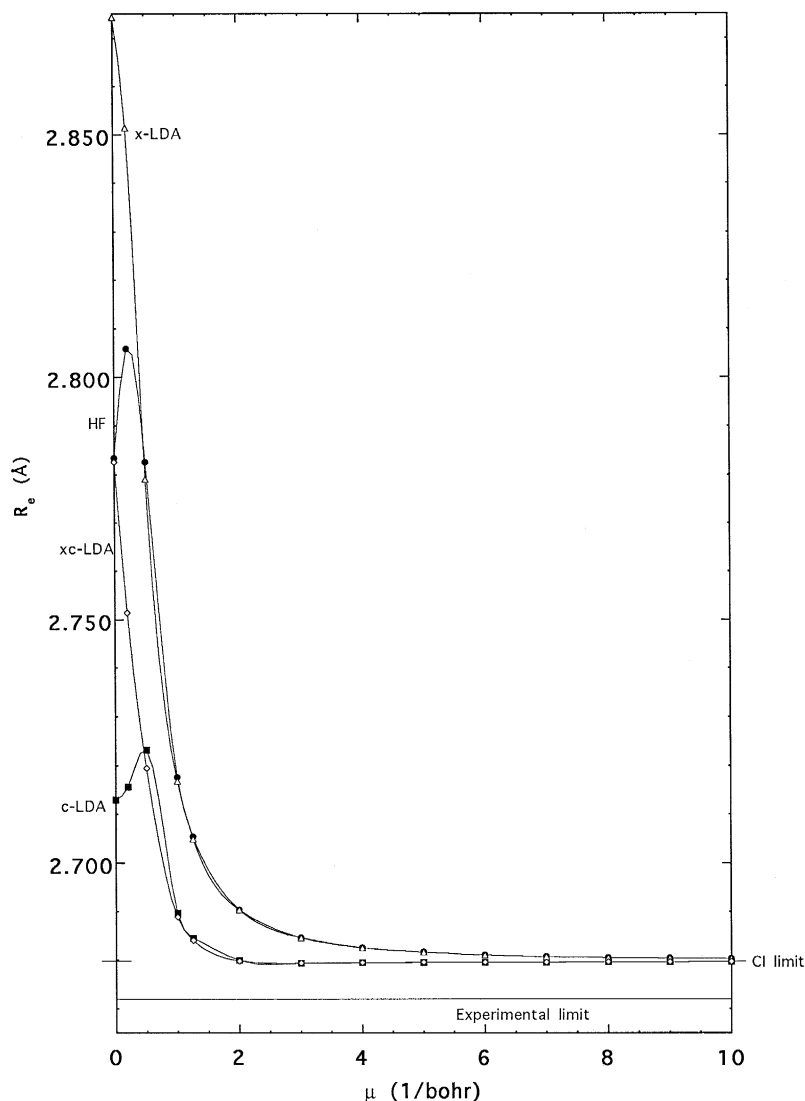


Fig. 4. Bond length R_e of Li_2 , for various short-range methods coupled to long-range CISD.

$\mu \in (2, \infty)$. D_e which is much too small (0.2 eV) at the SCF level and grossly overestimated with *c*-LDA (1.7 eV, when comparison is made to separate SCF atoms) converges even faster: $\Delta D_e < 0.05$ eV for $\mu > 0.5$. For all properties considered, the substantial differences between conventional *xc*-LDA and *c*-LDA calculations virtually disappear with DFT-CI coupling for $\mu > 0.5$. It should be mentioned that the

conclusions drawn here on the basis of pseudopotential calculations carry over, virtually without modification, to all-electron calculations.

F_2 is known as a particularly difficult molecule, with a stretched σ bond requiring multi-reference treatment (the single-reference CISD bond length is too small by 5 pm [24]), and unbound with respect to separate atoms at the SCF level. Accordingly, we

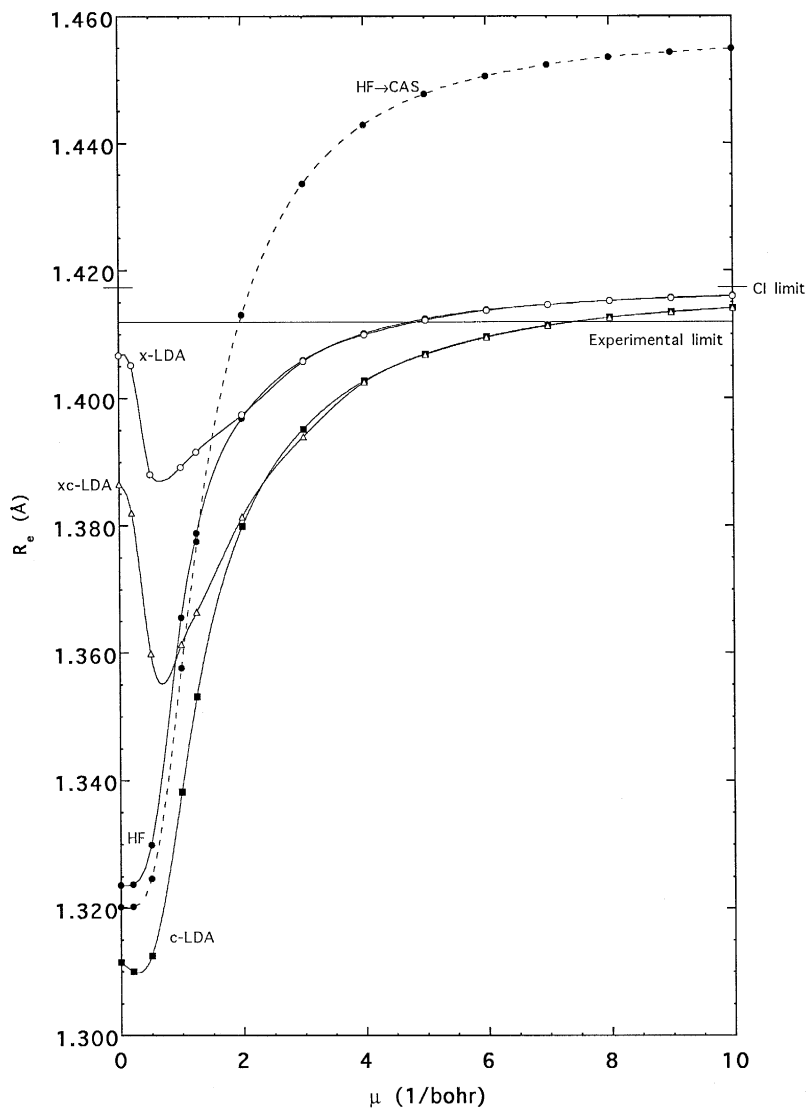


Fig. 5. Bond length R_e of F_2 , for various short-range methods coupled to long-range CASSCF/MRACPF (or CASSCF, in the case of the $HF \rightarrow CAS$ curve).

performed complete-active-space SCF (CASSCF) calculations, with $3\sigma_g$, $3\sigma_u$ as active orbitals, followed by multi-reference ACPF (MRACPF). The K shell of fluorine was replaced by an energy-consistent pseudopotential [25] and an optimized $6s6p$ valence basis set [27] with $2d1f$ polarization functions from Dunning's *vtz* set [26] was employed. Results for r_e , as a function of the DFT-CI screening parameter μ , are shown in Fig. 5. It is seen that the convergence to the full MRACPF limit for increasing μ is slower than for H_2 and Li_2 : even for $\mu = 4$, the deviation from the experimental bond length is around 1 pm. Of course, this is partly due to the F valence shell being more compact than for H or Li – the ratio of the atomic radii of Li and F is ~ 4 [21]. However, part of this behaviour has also to be attributed to the relatively slow convergence of non-dynamical correlation effects, cf. the 'HF \rightarrow CAS' curve in Fig. 5 which describes the transition from SCF to CASSCF as a function of μ . The density functionals are expected to account for (bond-shortening) dynamical correlation but cannot describe the large bond-lengthening near-degeneracy effect ($\Delta r_e = 14$ pm); they thus are at a disadvantage against the pure long-range CI (HF curve in Fig. 5) which exhibits an error compensation between missing short-range dynamical and static correlation. For the dissociation energy, calculated with respect to the sum of conventional ACPF atomic energies, the situation is more favourable for the DFT-CI coupling, since static and dynamical correlation contributions are of the same sign. In fact, cf. Table 1, both *xc*-LDA and *c*-LDA are much more accurate here than the pure long-range CI (labelled HF in Table 1). As in the case of H_2 , the non-spin-polarized

density functionals work remarkably well even in the case of dissociation ($r \rightarrow \infty$) so that the dissociation energy when calculated as the difference between $E^\mu(r)$ and $E^\mu(\infty)$, for a given μ , is accurate to 0.2 eV for $\mu = 4$ with both *xc*-LDA and *c*-LDA, see Table 1.

Results for dissociation energies of C_2 and N_2 , from single-point full-valence-space CASSCF-MRACPF calculations at the experimental r_e , are also shown in Table 1. Again, energy-consistent pseudopotentials [25] are used, together with even-tempered $10s10p$ valence basis sets and the $3d2f1g$ *vtz* polarization sets from Ref. [26]. The situation for $D_e(C_2)$ is similar to F_2 , whereas in the case of N_2 the high-spin atomic limit seems to deteriorate somewhat the convergence of D_e with μ , when reference is made to atoms at $r \rightarrow \infty$, calculated with the same non-spin-polarized DFT-CI coupling as for the molecule. The basis-set dependence, as judged from the difference between D_e values with *vdz* and *vtz* polarization sets, is 0.1 (0.5) eV and 0.1 (0.8) eV for C_2 and N_2 at $\mu = 2$ ($\mu \rightarrow \infty$), when reference is made to conventional ACPF atomic energies, $E^\mu(\infty)$; the corresponding $\mu = 2$ numbers for the $E^\mu(r_e)$ reference are 0.3 and 0.4 eV, respectively. A more complete discussion will be given elsewhere.

4. Conclusions

Density functionals for short-range electron–electron interaction can be used to effectively remove the need to describe correlation cusps with CI wavefunctions. It has been shown, using examples of closed-shell atoms (Be, Ne) and molecules (H_2 , Li_2 , C_2 ,

Table 1

Dissociation energies (eV) for various short-range methods coupled to long-range MRACPF, at selected values of the coupling parameter μ . In each case, the upper entry refers to $E^\mu(r_e) - E^\mu(\infty)$, the lower one to $E^\mu(r_e) - E^\mu(r_e)$. (Experimental values are 6.33, 9.90, and 1.69 eV for C_2 , N_2 , and F_2 , respectively)

μ	C_2		N_2		F_2		
	2	4	2	4	2	4	
HF	4.06	5.59	6.24	6.11	9.68	−5.34	1.55
	6.36	6.26	6.24	11.21	9.68	2.16	1.55
<i>c</i> -LDA	5.80	6.21	6.24	9.25	9.68	1.45	1.55
	6.61	6.36	6.24	11.64	9.68	2.30	1.55
<i>xc</i> -LDA	5.95	6.22	6.24	9.63	9.68	3.23	1.55
	6.63	6.36	6.24	11.53	9.68	2.19	1.55

N_2 , F_2), that a simple short-range LDA, depending on the total density only, gives quite a reliable account of dynamical correlation, so that usually only a moderate portion of explicitly (CI-like) treated long-range interaction has to be mixed in. While the results in this regime are more accurate than with pure DFT, one-particle/many-particle basis-set requirements are less severe than with pure CI. Further improvements, currently underway in our laboratory, include accounting for spin polarization and developing gradient-corrected short-range density functionals.

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