PHYSICAL REVIEW A, VOLUME 66, 012504

# Coupled-cluster calculations using local potentials

C. Gutlé,[1] J. L. Heully,[2] J. B. Krieger,[3] and A. Savin[4]
[1]*Laboratoire de Chimie Théorique, CNRS and Université Pierre et Marie Curie, F-75252 Paris, France*
[2]*Laboratoire de Physique Quantique, Univerité Paul Sabatier, F-31062 Toulouse, France*
[3]*Physics Department, Brooklyn College, CUNY, Brooklyn, New York 11210*
[4]*Laboratoire de Chimie Théorique, CNRS and Université Pierre et Marie Curie, F-75252 Paris, France*

(Received 28 December 2001; revised manuscript received 19 March 2002; published 19 July 2002)

Coupled-cluster calculations starting from exchange-only local-density approximation (XLDA), Krieger-Li-Iafrate (KLI), and Kohn-Sham (KS) wave functions are compared with those using the Hartree-Fock (HF) determinant as a reference. The total energies are found to be close, the difference being maximally 2 mhartree in the systems studied (the first terms in the He, Be, Ne, Mg, Ar isoelectronic series). The convergence is, however, sensitive to the choice of the reference: KLI and KS converge, in general, faster than HF in spite of being a worse approximation in the first two orders of perturbation theory. The improvement of convergence due to the use of the KLI or KS references is more pronounced in the systems showing near degeneracy, such as in the Be series. For XLDA, the convergence properties are either comparable to those of KLI or oscillatory, depending on the system. In a second part, the numerical results are analyzed (in the HF and KLI cases) by using first-order developments with respect to nuclear charge $Z$ at large $Z$.

DOI: 10.1103/PhysRevA.66.012504 PACS number(s): 31.25.Eb, 31.15.Dv, 31.15.Md, 02.60.Cb

## I. INTRODUCTION

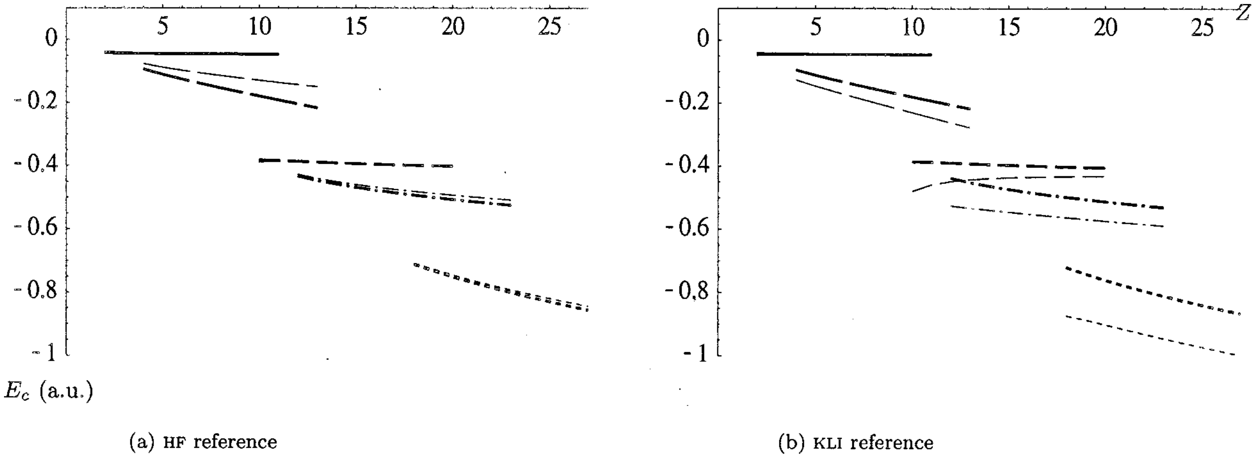
Usually, many-body calculations are performed using the Hartree-Fock operator as a single-particle reference, since this method yields the energetically lowest one-determinant guess for the wave function; in addition, it benefits from the Brillouin theorem as a technical simplification. However, it is well known that Hartree-Fock (HF) orbitals very poorly describe excited states. Kelly [1] has recognized the importance of the choice of virtual orbitals in calculating the correlation energy, and proposed to use the Hartree-Fock orbitals of the system with one electron removed. Davidson [2] has further analyzed the role of the virtual orbitals in perturbation theory by partitioning differently the Hamiltonian such that the reference Hartree-Fock determinant is rotated through unitary transforms. Alternatively, the Kohn-Sham (KS) potential seems to have a convenient ordering of virtual states (see, e.g., [3]). It has been proposed by Fritsche [4] to use the KS wave function as a reference for correlated calculations. This choice ensures, in addition, the exact density at zeroth order. Görling and Levy [5] developed a perturbation theory for the correlation energy, where the external potential is constrained to keep the ground-state density correct at each order. The KS potential is, however, not known in general. As a first approximation to it, it seems reasonable to use the optimized effective potential (see, e.g., the work of Talman and Shadwick [6], or more recently Engel and coworkers [7,8]), or the Krieger-Li-Iafrate (KLI) [9] approximation to this exact-exchange potential (see, e.g., Engel *et al.* [10] for application to molecules). Exact-exchange Kohn-Sham methods [11] have been used too. Moreover, using the KLI potential is consistent with density-functional theory schemes if we prospect further for methods coupling wave function with density [12]. Shankar and Narasimhan [13,14] have performed correlated calculations using orbitals obtained in the $X_\alpha$ local approximation. More recently, calculations have been performed using approximate density-functional potentials [15,16]. $X_\alpha$ and KLI potentials are quite different in the asymptotic region, the first decaying exponentially, the last proportional to $1/r$ (for neutral systems). Thus, the virtual orbitals are expected to be quite different in the two approximations.

In preceding papers [17,18], we made preliminary calculations at the level of second order perturbation theory using KLI and KS orbitals in Slater basis sets. In the present paper, we go further with numerical coupled-cluster calculations using singly and doubly excited states (CCSD) and compare the results obtained starting with orbitals from the exchange-only local-density approximation (XLDA) and KLI method to those obtained with HF orbitals. When possible, comparisons with KS wave functions were also made. The final part of the paper discusses the dependence of the correlation energy upon the nuclear charge $Z$ (in the large $Z$ limit) and upon the choice of the unperturbed system (HF, KLI). Concerning the second point, we noticed a difference of sensitivity upon the potential in the approximation used (CCSD or second-order of perturbation theory). We would like to point out that the problem mentioned by Bonetti *et al.* [19] is of no importance here: while they use second-order perturbation theory to construct a local potential, we make correlated calculations starting with a given potential.

## II. COUPLED-CLUSTER CALCULATIONS

### A. Technical details

The systems under investigation here are chosen to be closed-shell atoms and their first isoelectronic cations because accurate numerical calculations in that field are feasible, using the nonrelativistic CCSD program by Salomonson and co-workers [20]. Furthermore, the behavior of these series with nuclear charge $Z$ is known from Linderberg and Shull [21] and finally we possess very precise estimations of the exact correlation energies by Chakravorty *et al.* [22] to be compared with.



(a) HF reference (b) KLI reference

FIG. 1. Second-order and coupled-cluster correlation energies $E_c$ as a function of the nuclear charge $Z$. Thin line, second order; thick line, coupled clusters; full line, He series ($Z \in [2,11]$); long dashed line, Be series ($Z \in [4,13]$); dashed line, Ne series ($Z \in [10,20]$); dashed dotted line, Mg series ($Z \in [12,23]$); dotted line, Ar series ($Z \in [18,27]$). Note that in the HF case, the second-order and coupled-cluster curves are almost indistinguishable at the scale of the figure, except for the Be series. Same remark for the He series in the KLI case.

The HF and XLDA potentials are obtained from the nonrelativistic self-consistent-field program [23], and the KLI potentials from the Li program [24]. The KS potentials were generated by Colonna and co-workers [25,26] (in the He and Be series) and Filippi *et al.* [27] (for the neon atom).

In the numerical coupled-cluster program [20], we included all the single and double excitations giving nonzero contributions in a multipole expansion of $1/r_{12}$ as a sum of spherical harmonics products up to angular momentum $l = 14$. We used 200 orbitals per symmetry so that the valence and Rydberg states are well described, as we expected the KLI potential to produce more bounded states than the HF potential does. The potentials were projected on an exponential grid of a thousand points scaled with the nuclear charge $Z$ and the number of electrons in the system. We expect for our results the numerical accuracy of a few tenths of mhartrees in the He, Be, and Ne series and 1 mhartree in the Mg and Ar series. They are given without radial or angular extrapolations as we estimate this effect to be below 0.1 mhartree and thus irrelevant for the purpose of our paper, which is the comparison between different potentials.

### B. Energies

In this section, we present our results for the energies and correlation energies. First, we comment on the effect of changing the nuclear charge in a series (system-specific point of view) while keeping the same variant of potential (HF, XLDA, KLI, or KS) for the calculations. Then we specify to a given system and vary the type of potential (reference-specific point of view). Some general trends are noted, to be commented in Sec. III (when HF and KLI potentials are used) with the help of a simplified model developed for that purpose.

#### *1. System-specific point of view*

In Fig. 1, the HF and KLI correlation energies $E_c$ are plotted with respect to nuclear charge $Z$, both at second-order perturbation theory and CCSD levels. At large $Z$, we observe that the correlation energies are nearly constant with $Z$ in the He and Ne series and linearly decreasing in the Be, Mg and Ar series. This behavior was expected for the exact correlation energy from Linderberg and Shull [21]. We find it here still valid in the approximations of second-order perturbation theory and coupled cluster. Furthermore, it is valid whatever the choice of the unperturbed Hamiltonian (HF, XLDA, and KLI). More precisely, in case of linearity (Be, Mg, Ar series), the slopes are ordered Be>Ar>Mg.

#### *2. Reference-specific point of view*

The numerical results are reported in Tables I and II for the He and Be series, respectively. Ne, Mg, and Ar series are available as supplementary data in Ref. [34]. If we consider a given system in one of these tables, the first row deals with HF reference, the second with XLDA, the third with KLI, and the fourth with KS reference (if the KS potential was available).

*a. Energies of the references*. The second column specifies the expectation values of the Hamiltonian ($E_{HF}$, $E_{XLDA}$, $E_{KLI}$, or $E_{KS}$) with different determinants (HF, XLDA, KLI, or KS, respectively) to be compared now. We expected $E_{HF}$ to be smaller or equal to $E_{XLDA}$, $E_{KLI}$, and $E_{KS}$ by definition. In fact $E_{HF}$ and $E_{KLI}$ are found relatively close. $E_{HF} = E_{KLI}$ in the He series [9]; for the cases studied, we pointed out differences ($E_{KLI} - E_{HF}$) up to 1 mhartree in the Be series, of 2↪3 mhartree in the Ne series (we will present the results as $x \hookrightarrow y$, where $x$ corresponds to the beginning of the series, and $y$ to the end), 4↪5 mhartree in the Mg series, and 7↪8 mhartree in the Ar series. A slight increase of $E_{KLI} - E_{HF}$ with nuclear charge is present; it is however expected to disappear as $Z \rightarrow \infty$. $E_{KS} - E_{HF}$ is larger than $E_{KLI} - E_{HF}$. It is probably due to a constraint of exact density added to that of locality ($E_{KS} - E_{HF}$ is 0.03↪0.07 mhartree in the He series, 2↪12 mhartree in the Be series). This difference has been used by Valderrama *et al.* [28] to define

TABLE I. Total energies in the He series (a.u.). Consider a given nuclear charge ($Z$) in the first column. We present the (monodeterminantal) first-order energy ($E_V$) in the second column, the second-order energy ($E_V^{(2)}$) in the third column, the third-order energy ($E_V^{(3)}$) in the fourth column, the coupled-cluster energy ($E_{CCSD(V)}$) in the fifth column, and an estimation of the exact total energy ($E_{exact}$) [22] in the sixth column. $V$ specifies the potential used for the calculation: $V=$HF in the first row, XLDA in the second row, KLI in the third row (and KS in the fourth row when it was available).

| $Z$ | $E_V$ | $E_V^{(2)}$ | $E_V^{(3)}$ | $E_{CCSD(V)}$ | $E_{exact}$ |
|---|---|---|---|---|---|
| 2 (HF) | −2.8617 | −2.8990 | −2.9009 | −2.9037 | −2.9037 |
| (XLDA) | −2.8578 | −2.9125 | −2.9053 | −2.9037 | |
| (KLI) | −2.8617 | −2.9100 | −2.9056 | −2.9037 | |
| (KS) | −2.8616 | −2.9101 | −2.9056 | −2.9037 | |
| 3 | −7.2364 | −7.2766 | −7.2780 | −7.2799 | −7.2799 |
| | −7.2330 | −7.2851 | −7.2814 | −7.2799 | |
| | −7.2364 | −7.2839 | −7.2813 | −7.2799 | |
| | −7.2364 | −7.2840 | −7.2813 | −7.2799 | |
| 4 | −13.6113 | −13.6530 | −13.6541 | −13.6556 | −13.6556 |
| | −13.6080 | −13.6592 | −13.6567 | −13.6556 | |
| | −13.6113 | −13.6585 | −13.6566 | −13.6556 | |
| | −13.6113 | −13.6586 | −13.6566 | −13.6556 | |
| 5 | −21.9862 | −22.0289 | −22.0298 | −22.0310 | −22.0310 |
| | −21.9830 | −22.0338 | −22.0319 | −22.0310 | |
| | −21.9862 | −22.0333 | −22.0318 | −22.0310 | |
| | −21.9862 | −22.0333 | −22.0318 | −22.0310 | |
| 6 | −32.3612 | −32.4045 | −32.4053 | −32.4062 | −32.4062 |
| | −32.3580 | −32.4086 | −32.4070 | −32.4062 | |
| | −32.3612 | −32.4082 | −32.4070 | −32.4062 | |
| | −32.3612 | −32.4082 | −32.4069 | −32.4062 | |
| 7 | −44.7362 | −44.7799 | −44.7806 | −44.7814 | −44.7814 |
| | −44.7330 | −44.7834 | −44.7821 | −44.7814 | |
| | −44.7362 | −44.7831 | −44.7821 | −44.7814 | |
| | −44.7361 | −44.7831 | −44.7820 | −44.7814 | |
| 8 | −59.1111 | −59.1552 | −59.1559 | −59.1566 | −59.1566 |
| | −59.1080 | −59.1583 | −59.1572 | −59.1566 | |
| | −59.1111 | −59.1580 | −59.1571 | −59.1566 | |
| | −59.1111 | −59.1580 | −59.1571 | −59.1566 | |
| 9 | −75.4861 | −75.5305 | −75.5311 | −75.5317 | −75.5317 |
| | −75.4830 | −75.5332 | −75.5323 | −75.5317 | |
| | −75.4861 | −75.5330 | −75.5322 | −75.5317 | |
| | −75.4861 | −75.5330 | −75.5322 | −75.5317 | |
| 10 | −93.8611 | −93.9057 | −93.9062 | −93.9068 | −93.9068 |
| | −93.8580 | −93.9082 | −93.9073 | −93.9068 | |
| | −93.8611 | −93.9080 | −93.9072 | −93.9068 | |
| | −93.8611 | −93.9079 | −93.9072 | −93.9068 | |
| 11 | −114.2361 | −114.2809 | −114.2814 | −114.2819 | −114.2819 |
| | −114.2330 | −114.2831 | −114.2823 | −114.2819 | |
| | −114.2361 | −114.2829 | −114.2823 | −114.2819 | |

TABLE II. Total energies in the Be series (a.u.). Same legend as in Table I.

| $Z$ | $E_V$ | $E_V^{(2)}$ | $E_V^{(3)}$ | $E_{CCSD(V)}$ | $E_{exact}$ |
|---|---|---|---|---|---|
| 4 | −14.5730 | −14.6493 | −14.6538 | −14.6668 | −14.6674 |
| | −14.5723 | −14.6983 | −14.6713 | −14.6667 | |
| | −14.5681 | −14.6997 | −14.6712 | −14.6667 | |
| | −14.5712 | −14.7022 | −14.6710 | −14.6667 | |
| 5 | −24.2376 | −24.3254 | −24.3314 | −24.3482 | −24.3489 |
| | −24.2367 | −24.3824 | −24.3556 | −24.3481 | |
| | −24.2326 | −24.3841 | −24.3557 | −24.3481 | |
| | −24.2350 | −24.3893 | −24.3547 | −24.3482 | |
| 6 | −36.4085 | −36.5059 | −36.5134 | −36.5341 | −36.5349 |
| | −36.4075 | −36.5711 | −36.5435 | −36.5340 | |
| | −36.4035 | −36.5731 | −36.5436 | −36.5340 | |
| | −36.4047 | −36.5830 | −36.5414 | −36.5341 | |
| 7 | −51.0823 | −51.1883 | −51.1973 | −51.2219 | −51.2229 |
| | −51.0813 | −51.2620 | −51.2330 | −51.2218 | |
| | −51.0773 | −51.2642 | −51.2332 | −51.2219 | |
| | −51.0771 | −51.2816 | −51.2288 | −51.2220 | |
| 8 | −68.2577 | −68.3716 | −68.3820 | −68.4107 | −68.4118 |
| | −68.2566 | −68.4539 | −68.4234 | −68.4106 | |
| | −68.2527 | −68.4563 | −68.4236 | −68.4107 | |
| | −68.2506 | −68.4848 | −68.4153 | −68.4110 | |
| 9 | −87.9341 | −88.0555 | −88.0674 | −88.1001 | −88.1012 |
| | −87.9330 | −88.1465 | −88.1143 | −88.1000 | |
| | −87.9291 | −88.1491 | −88.1145 | −88.1000 | |
| | −87.9249 | −88.1907 | −88.1005 | −88.1004 | |
| 10 | −110.1110 | −110.2396 | −110.2530 | −110.2898 | −110.2910 |
| | −110.1099 | −110.3396 | −110.3054 | −110.2897 | |
| | −110.1060 | −110.3423 | −110.3057 | −110.2897 | |
| | −110.0991 | −110.4043 | −110.2801 | −110.2904 | |
| 11 | −134.7884 | −134.9240 | −134.9389 | −134.9798 | −134.9810 |
| | −134.7873 | −135.0329 | −134.9968 | −134.9796 | |
| | −134.7834 | −135.0358 | −134.9971 | −134.9797 | |
| 12 | −161.9661 | −162.1085 | −162.1249 | −162.1699 | −162.1711 |
| | −161.9649 | −162.2264 | −162.1884 | −162.1697 | |
| | −161.9611 | −162.2295 | −162.1887 | −162.1698 | |
| 13 | −191.6440 | −191.7931 | −191.8110 | −191.8601 | −191.8613 |
| | −191.6428 | −191.9200 | −191.8800 | −191.8600 | |
| | −191.6390 | −191.9234 | −191.8804 | −191.8600 | |

near degeneracy. $E_{XLDA}-E_{HF}$ is also more important: $4\hookrightarrow 3$ mhartree in the He series, 5 mhartree in the Be series, $20\hookrightarrow 11$ mhartree in the Ne series, $17\hookrightarrow 13$ mhartree in the Mg series, $22\hookrightarrow 20$ mhartree in the Ar series.

*b. Total energies*. At this stage, it would be usual to present the correlation energies. The definition is, however, not unique in our case. It is most often defined in *ab initio* approaches as the difference between the exact nonrelativistic and Hartree-Fock energies [29], but in density-functional theory, $E_{KS}$ is used instead of $E_{HF}$ (see, e.g., Levy [30]); $E_{XLDA}$ [13] or $E_{KLI}$ [12] can be used as well. In order to compare the results obtained starting from different references, we present in the tables the total energies. For a given system, the following levels of approximation are reported: second and third orders of perturbation theory ($E_V^{(2)}$ and $E_V^{(3)}$) in columns 3 and 4, respectively, coupled cluster ($E_{CCSD(V)}$) in column 5 and exact ($E_{exact}$) estimation [22] in column 6. We recall that the potentials $V$ used are HF in the first row, XLDA in the second, KLI in the third, and KS in the fourth.

The second-order total energies are found extremely sensitive to the potential used (see column 3 and Fig. 1).

As a rule, the second-order energies based on XLDA, KLI, and KS are lying much below those obtained with HF. The differences $E_{HF}^{(2)}-E_{KLI}^{(2)}$ range in $11\hookrightarrow 2$ mhartree in the He series, $49\hookrightarrow 127$ mhartree in the Be series, $89\hookrightarrow 28$ mhartree in the Ne series, $94\hookrightarrow 75$ mhartree in the Mg series, and $158\hookrightarrow 144$ mhartree in the Ar series. With the XLDA potential, the second-order energies are even lower than those with KLI or KS. $E_{HF}^{(2)}-E_{XLDA}^{(2)}$ ranges in $13\hookrightarrow 22$ mhartree in the He series, $50\hookrightarrow 130$ mhartree in the Be series, $119\hookrightarrow 30$ mhartree in the Ne series $106\hookrightarrow 78$ in the Mg series, and $166\hookrightarrow 148$ in the Ar series. Third-order perturbation theory (see column 4) slightly lessens the above differences. For instance, $E_{HF}^{(3)}-E_{KLI}^{(3)}$ spans $4.7\hookrightarrow 1$ mhartree in the He series, $17\hookrightarrow 69$ mhartree in the Be series, $19\hookrightarrow 10$ mhartree in the Ne series, $25\hookrightarrow 29$ mhartree in the Mg series, and $37\hookrightarrow 42$ mhartree in the Ar series.

In striking contrast to second and third orders, the agreement between coupled-cluster results starting from different references is very good (see column 5). This is of course not surprising, taking into account Thouless's theorem [31]. Of course, the choice of the reference is immaterial in the He series, as CCSD is exact for two-electron systems. However, as electrons are added to the system and higher-order excitations omitted (triple, quadruple, etc.), CCSD is expected to stray from the full configuration interaction (CI). As a consequence, different choices for the reference should no longer be strictly equivalent: In fact, $E_{CCSD(HF)}$ and $E_{CCSD(KLI)}$ are found to differ by $0\hookrightarrow -0.2$ mhartree in the Be series, $2\hookrightarrow 0.2$ mhartree in the Ne series, $0.5\hookrightarrow -0.2$ mhartree in the Mg series, and $0.8\hookrightarrow 0.4$ mhartree in the Ar series. $E_{CCSD(HF)}-E_{CCSD(XLDA)}$ is zero in the Be series, $1\hookrightarrow 0.1$ mhartree in the Ne series, $0.2\hookrightarrow -0.2$ mhartree in the Mg series, and $0.1\hookrightarrow 0.4$ mhartree in the Ar series.

Concerning the absolute accuracy of the CCSD method, the CCSD(HF), CCSD(XLDA), and CCSD(KLI) calculations are compared to the estimated exact values [22]. As expected, all values are identical in the He series. The discrepancies with respect to the exact values are $-0.7\hookrightarrow -1.4$ mhartree in the Be series, $-9.5\hookrightarrow -0.7$ mhartree in the Ne series ($-9.5$ mhartree for the Ne atom), $-6.8\hookrightarrow -2.7$ mhartree in the Mg series, and $-14.8\hookrightarrow -3.0$ mhartree in the Ar series. By comparing $E_{CCSD(HF)}-E_{CCSD(KLI\ or\ XLDA)}$ with $E_{exact}-E_{CCSD(HF\ or\ KLI\ or\ XLDA)}$ given just above, we conclude that the absolute error of the CCSD method is in any case much more important (up to one order of magnitude) than the change induced by varying the reference between HF, XLDA, and KLI. This invariant indicates a compensatory role of the monoexcitations and diexcitations, the latter being still dominant (see Table III): the contribution from the monoexcitations to the correlation energy is below 1% with HF and KLI, it is below 10% with XLDA (in addition, it is generally found negative when the KLI and XLDA potentials are used, whereas it is always found positive with the HF potential). Thus, unfortunately, changing the reference potential in the CCSD procedure does not make up for the missing higher than double excitations. In a nutshell, it seems that $E^{(2)}$ is strongly reference dependent whereas $E_{CCSD}$ is not. Note that the same observation holds not only for the total energies, but also for the correlation energies (see Fig. 1). Moreover, it is to be noticed that the KS potential behaves quite similarly to KLI with respect to the preceding points.

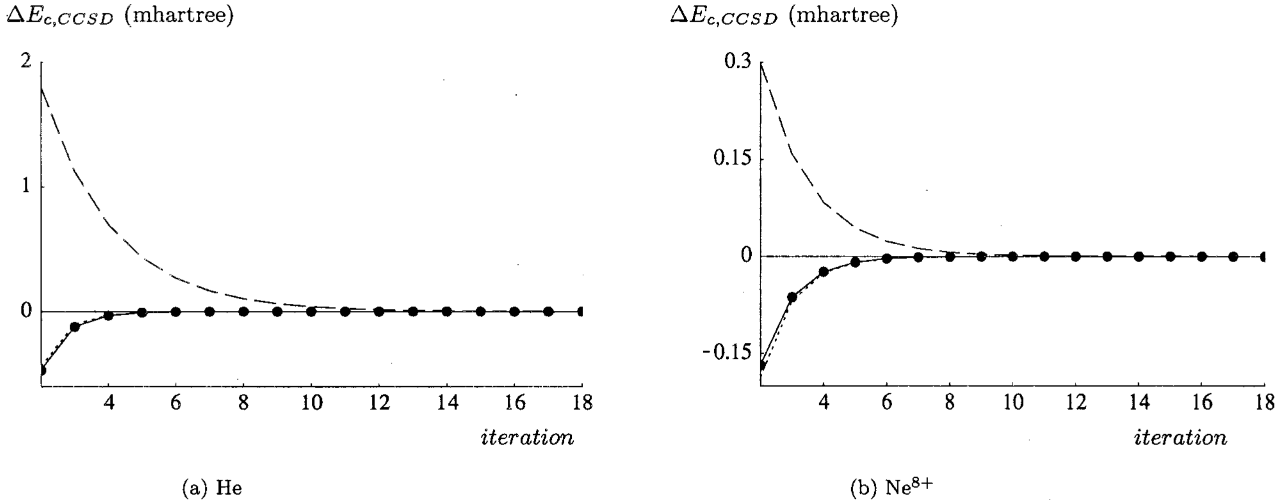
TABLE III. Percentage of monoexcitations in the correlation energies, using KLI, XLDA, and HF potentials in the He, Be, Ne, Mg, and Ar series. In the notation $x\hookrightarrow y$, $x$ designates the first and $y$ the last term of the series.

| Series | $E_{KLI}^{(2)}$ | $E_{CCSD(KLI)}$ | $E_{XLDA}^{(2)}$ | $E_{CCSD(XLDA)}$ | $E_{CCSD(HF)}$ |
|---|---|---|---|---|---|
| He | 0 | 0 | $10\hookrightarrow 6$ | $8\hookrightarrow 6$ | $-0$ |
| Be | $1\hookrightarrow 0$ | $1\hookrightarrow 0$ | $4\hookrightarrow 2$ | $5\hookrightarrow 2$ | $-0$ |
| Ne | $0\hookrightarrow 1$ | $0\hookrightarrow 1$ | $5\hookrightarrow 3$ | $4\hookrightarrow 3$ | $-0$ |
| Mg | 1 | 1 | $4\hookrightarrow 2$ | $3\hookrightarrow 2$ | $-0$ |
| Ar | 1 | 1 | $3\hookrightarrow 2$ | $3\hookrightarrow 2$ | $-0$ |

### C. Convergence

Those concerned with improving methodology in quantum chemistry are concerned with not only accuracy; the rapidity of convergence is also a valuable criterion. In the preceding section, we observed that CCSD calculations performed with HF, XLDA, KLI, and KS potentials were close. However, as will be seen below, they present very different convergence schemes. We plotted in Figs. 2–4 for the He, Be, and Ne series, respectively, the changes of the total energy during the coupled-cluster iterations, with respect to the converged value and when starting from different potentials (HF, KLI, XLDA; and KS when it was available). For the Mg and Ar series, see Ref. [34].

As a rule, (a) we observe that $E_{CCSD(HF)}$ is generally approached from above whereas $E_{CCSD(XLDA)}$ and $E_{CCSD(KLI)}$ are approached from below; (b) the convergence is usually significantly faster with KLI and KS than HF. In particular, the well-known pathological Be atom [32] is already converged to $10^{-5}$ a.u. at the third coupled-cluster iteration using KLI. By contrast, we should go up to iteration 29 using HF to get a comparably converged result. In order to understand point (a) we have to remember that the second-order perturbation theory was used as a guess for converging the numerical coupled-cluster equations iteratively. On the other hand, according to Tables I and II, tables from Ref. [34] for the Ne, Mg, and Ar series and Fig. 1, the relations $E_{HF}^{(2)}>E_{CCSD(HF)}$ and $E_{KLI}^{(2)}<E_{CCSD(KLI)}$ generally hold (with the exceptions of Ne, $Na^+$, and $Mg^{2+}$, where $E_{HF}^{(2)}<E_{CCSD(HF)}$). We have not studied in detail the source of the difference between the convergence behavior when using



(a) He

(b) $Ne^{8+}$

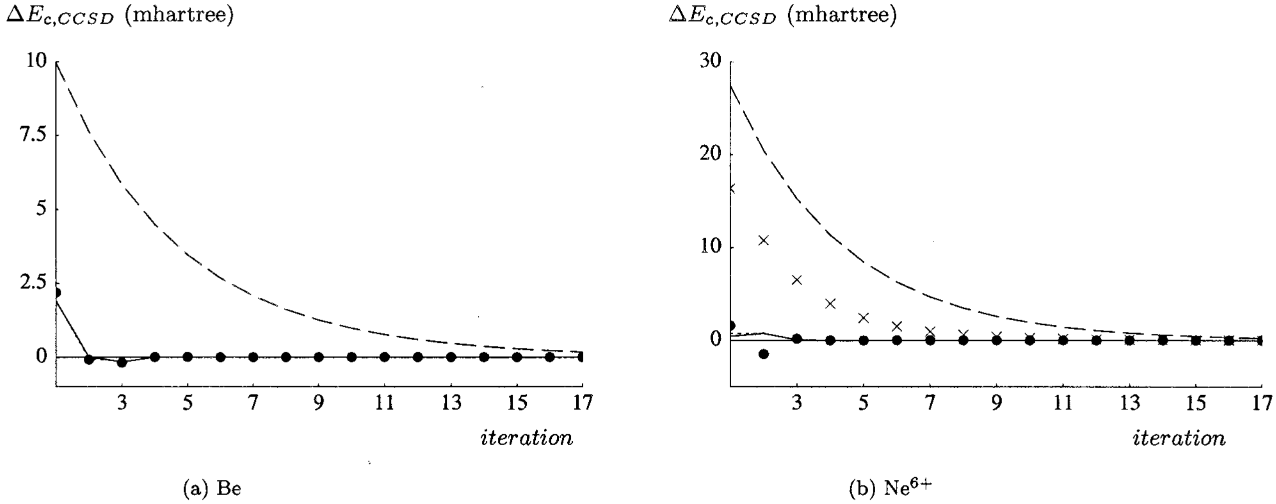
FIG. 2. Distance $\Delta E_{c,CCSD}$ to the coupled-cluster correlation energy $E_{c,CCSD}$ during the iterations; we used successively the HF (dashed line), XLDA (dotted line), KLI (full line), and KS (large dots) orbitals. Note that in the He series, the XLDA, KLI, and KS curves are superimposed below zero.

the HF or the KLI potentials [point (b)]. However, we would like to mention some thoughts on this subject. One possible explanation for the convergence behavior is the starting point, which is different in HF and KLI [point (a) above]. Another possible explanation is related to the energy denominators which appear when computing the corrections to the expansion coefficients of the wave function. As the difference between the occupied and unoccupied orbital energies $\Delta\epsilon$ is larger in HF than KLI, one may expect a smaller change from one iteration to the next in HF with respect to KLI. A further example going in this direction is the potential $V_{model}$ to be defined at Sec. III B 2 for $Ne^{6+}$. In that case, $\Delta\epsilon$ is intermediate between HF and KLI's. At the same time, the convergence curve of $V_{model}$ (see Fig. 3) lies between those of HF and KLI.

We add that the calculations based on the KS potential (for the cases treated here) behave quite similarly to those based on KLI, in contrast with HF. The calculations based on XLDA potential often behave similarly to those based on KLI, but an oscillatory convergence is observed in some cases (see Ne in Fig. 4).

## III. INTERPRETATION A LARGE *Z*

The energies were calculated in Sec. II B numerically, for different systems and by using different approximations. In order to refine our previous interpretation, we reinvestigate here the same calculations, analytically and at large *Z*. Linderberg and Shull [21] have already performed a *Z* expansion of the full-CI equations. They showed that for some



(a) Be

(b) $Ne^{6+}$

FIG. 3. Four-electron systems (same legend as in Fig. 2). $V_{model}$ potential of Sec. III B 2 is marked with crosses (only for $Ne^{6+}$). Note that in the Be series, the XLDA, KLI, and KS curves are superimposed.

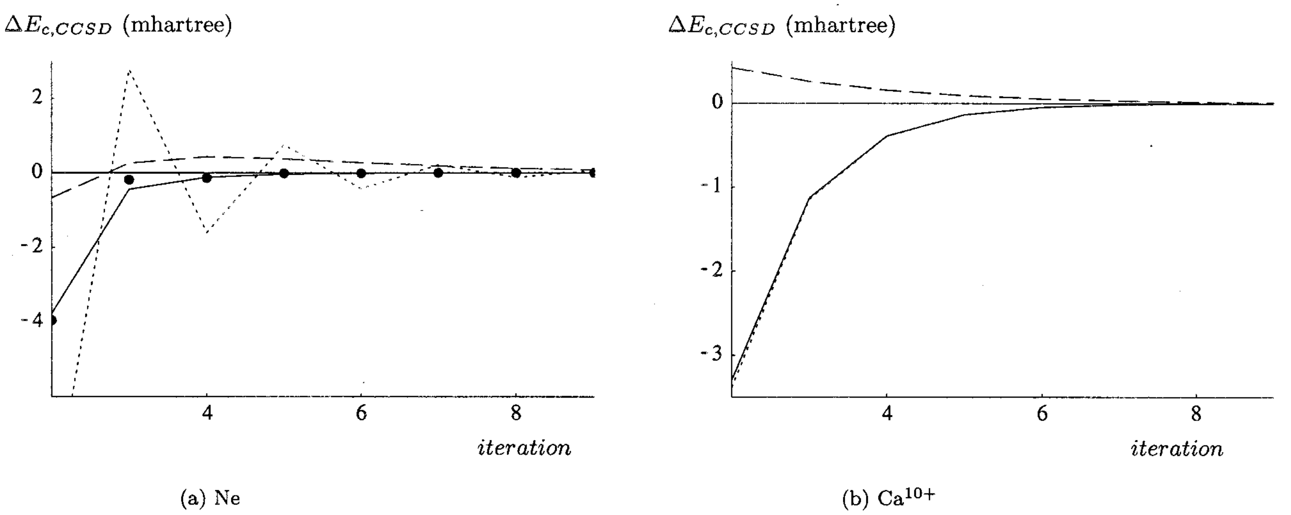


FIG. 4. Ten-electron systems (same legend as in Fig. 2, except KS for Ca$^{10+}$ not available). Note that for Ca$^{10+}$, the XLDA and KLI curves are superimposed.

systems where near degeneracy is present (Be, Mg, and Ar series in our case), the exact correlation energy has a principal contribution linear with $Z$ at large $Z$. By contrast, in closed-shell systems (He and Ne series in our case) this term is zero and the next one in the development a constant. Our purpose now is to follow the same procedure in case of approximate methods for calculating the correlation energies (perturbation theory and coupled cluster based on different potentials) and see to what extent the results are changed. HF and KLI will be discussed in the present. Only the conclusions are reported in Secs. III A and III B; for more details the reader is referred to Appendixes A and B [35]. We caution the reader that in this section all the energies are discussed in atomic units to make the comparisons with Sec. II easier. However, the corresponding appendixes are mostly concerned with modified hartree units as they are more convenient for developments with $Z$.

### A. A unique reference for defining the correlation energy to first order in Z

In Sec. II B 2, we compared the total energies $E$ obtained with different potentials instead of discussing the correlation energies $E_c$, as more usually done in quantum chemistry. The reason for this choice was the nonuniqueness of the definition of the correlation energy when the model Hamiltonian is changed. However, in this section, we limit our analysis of the correlation energy at large $Z$ to first order in $Z$ as it will be sufficient to reproduce qualitatively most of the results of Sec. II B. Under this limitation, the correlation energy is uniquely defined. More precisely, the unique reference is found in Appendix A to be the $N$-hydrogenic system [36] with associated energy $\tilde{E}_{0,H}Z^2+\tilde{E}_0^{(1)}Z+\mathcal{O}(Z^0)$ ($\tilde{E}_{0,H}$ and $\tilde{E}_0^{(1)}$ given in Table IV). Thus, to first order in $Z$, the correlation energies may be compared in a series as well as the total energies, whatever the reference Hamiltonian.

### B. The correlation energy in approximate methods to first order in Z at large Z

#### 1. System-specific point of view

A general feature of the correlation energy within a series is the following. First, it has no quadratic component in $Z$. Then, the linear coefficient in $Z$ can only result from intravalence excitations in the hydrogenic spectrum [37] (cf. Appendix B). Thus, in closed-shell systems (He and Ne series), no $Z$-linear contribution to the correlation energy is expected (within these series, the first nonzero contributions should be a constant). This result is in accordance with our full calculations (see, for instance, Fig. 1 for $V=V_{HF}$ and $V_{KLI}$): the second-order and CCSD correlation energies are nearly constant within the He and Ne series, at least at large $Z$. By contrast, in incomplete shells and closed subshells (Be, Mg, Ar series), where near degeneracy is present, the correlation energy has a nonzero $Z$ coefficient leading to the mainly $Z$-linear (at large $Z$) curves plotted in Fig. 1, both in coupled-cluster and second-order perturbation theory approximations. The corresponding $Z$-linear coefficients are also given in Table V in second-order perturbation theory to be compared with the exact ones estimated by Chakravorty *et al.* [22]. In particular, we note that the slopes are ordered Be<Ar<Mg, as observed in the calculations reported in Sec. II. Furthermore, these $Z$-linear contributions are due to diexcitations

TABLE IV. $Z$-quadratic $\tilde{E}_{0,H}$ and linear $\tilde{E}_0^{(1)}$ components of the monodeterminantal ground-state energy (in a.u.) in the He, Be, Ne, Mg, and Ar series.

| Series | $\tilde{E}_{0,H}$ | $\tilde{E}_0^{(1)}$ |
|---|---|---|
| He | $-1$ | 0.625 |
| Be | $-1.25$ | 1.571001 |
| Ne | $-2$ | 8.770830 |
| Mg | $-2.111111$ | 10.567378 |
| Ar | $-2.444444$ | 17.980333 |

TABLE V. Exact $Z$-linear component of the correlation energy (in a.u.): column 1, series; column 2, second-order perturbation theory (KLI reference); column 3, valence CI [22]; column 4, second-order perturbation theory (HF reference).

| Series | $\tilde{E}^{(2)}_{KLI}$-$\tilde{E}_0$ | $\tilde{E}_c$ | $\tilde{E}^{(2)}_{HF}$-$\tilde{E}_0$ |
|---|---|---|---|
| He | 0 | 0 | 0 |
| Be | $-0.015356$ | $-0.011727$ | $-0.005981$ |
| Ne | 0 | 0 | 0 |
| Mg | $-0.004270$ | $-0.003574$ | $-0.002473$ |
| Ar | $-0.008642$ | $-0.006927$ | $-0.005704$ |

only, all monoexcitations in the valence space being zero due to angular symmetries. This property is not only satisfied in the series studied, it is specific to spherically symmetric systems (cf. Appendix D).

### *2. Reference-specific point of view*

In the presence of near degeneracy, the approximate methods fall into two categories (see Appendixes A and B for details): (a) the methods depending on the choice of the potential to first order in $Z$ (for instance, a finite-order perturbation theory), (b) the methods independent of the potential to first order in $Z$ (for instance, coupled cluster or truncated CI, provided the criterion for the truncation is not chosen to depend upon a model Hamiltonian). Notice that if perturbation theory (a) is pushed on as far as infinite order, and if it converges to the exact result, it should of course become independent of the potential.

For second-order perturbation theory [type (a)] the inequalities $E^{(2)}_{HF} > E_{\text{exact}} > E^{(2)}_{KLI}$ are satisfied to first order in $Z$ in the Be, Mg, and Ar series, as already observed in the full calculations of Sec. II. According to Sec. III A, the same holds for the correlation energies (see Table V). Actually, the first order in $Z$ Møller-Plesset-like expression for the correlation energy (derivation in Appendix B)

$$Z \sum_{D}^{valence} \frac{|\langle \tilde{\Phi}_{0,H} | \sum_{i<j} \frac{1}{r_{ij}} | \tilde{\Phi}_{D,H} \rangle|^2}{\Delta \tilde{\epsilon}^{(1)}_{D,m}} + \mathcal{O}(Z^0) \qquad (1)$$

has a dependence upon the model Hamiltonian only through the linear components of the valence energy gaps $\Delta\tilde{\epsilon}^{(1)}_{D,m}$ (the numerator matrix elements only involve Slater determinants based on hydrogenic orbitals: the ground state $\tilde{\Phi}_{0,H}$ and intravalence diexcitations $\tilde{\Phi}_{D,H}$). The relevant $\Delta\tilde{\epsilon}^{(1)}_{D,m}$ are given in Table VI for the Be, Mg, and Ar series. For all these systems, the energy gaps in the valence space are found smaller with KLI than HF potential. The difference may be attributed to the asymptotic behaviors of these potentials, as $r \rightarrow \infty$. Namely, at large $Z$, the HF potential has the physically correct (attractive) asymptote $[-(Z-N+1)]/r$ for the occupied orbitals and the too repulsive behavior $-(Z-N)/r$ for the virtuals, resulting in too large gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orital (LUMO); on the contrary, KLI has the unique (as it is local) attractive asymptote $[-(Z-N+1)]/r$, resulting in smaller HOMO-LUMO gaps. For example, consider the $2s$-$2p$ energy gap for $\text{Ne}^{6+}$: it represented in the full calculations of Sec. II, 658 mhartree with KLI versus 1713 mhartree with HF. To first order in $Z$, we obtain the same relative orders of magnitude: 838 mhartree with KLI versus 2152 mhartree with HF. The sensitivity of the methods (a) on the orbital energies suggests, in particular, the existence of a potential producing energy gaps intermediate between those of HF and KLI and yielding the exact correlation energy already at second-order perturbation theory. As an illustration, let us construct such a potential for $\text{Ne}^{6+}$, by using an arbitrary prescription. Consider a class of potentials satisfying

TABLE VI. $Z$-linear contributions to the valence energy gaps $\Delta\tilde{\epsilon}^{(1)}_{D,m}$ (in a.u.) in the Be, Mg, and Ar series using KLI and HF potentials.

| Series | Excitation | $\Delta\tilde{\epsilon}^{(1)}_{D,KLI}$ | $\Delta\tilde{\epsilon}^{(1)}_{D,HF}$ |
|---|---|---|---|
| Be | 2s→2p | 0.083841 | 0.215252 |
| Mg | 3p→3s | 0.075034 | 0.131543 |
|  | 3d→3s | 0.177976 | 0.254918 |
| Ar | 3s→3d | 0.234040 | 0.320602 |
|  | 3p→3d | 0.141209 | 0.214558 |

$$V_{model}(r) = 10^2 \left[ -\frac{1}{10r} + \frac{1}{10} \tilde{V}^{(1)}_{KLI}(10r) + a e^{-(10r-b)^2} \right], \qquad (2)$$

where $\tilde{V}^{(1)}_{KLI}$ is defined by Eq. (C5) of Appendix C and $a$ and $b$ are parameters. For $Z=10$, $10^2[-1/(10r) + 1/10\tilde{V}^{(1)}_{KLI}(10r)]$ obtained via hydrogenic orbitals is a relatively good approximation to $V_{KLI}$. As seen in Fig. 5, the approximate $V_{KLI}$ has practically reached its asymptote for $r=1$ a.u. The densities of the $2s$ and $2p$ hydrogenic orbitals being maximal for $10r=5.236\,07$ and 4. a.u., respectively, we understand that $V_{KLI}$ has roughly the same attractive behavior upon these two orbitals, resulting in a too small HOMO-LUMO gap and a too strong total energy at second-order peturbation theory, as discussed above. One idea for increasing the HOMO-LUMO gap would be to add an attractive component to $V_{KLI}$ acting on $2s$ specifically, and letting

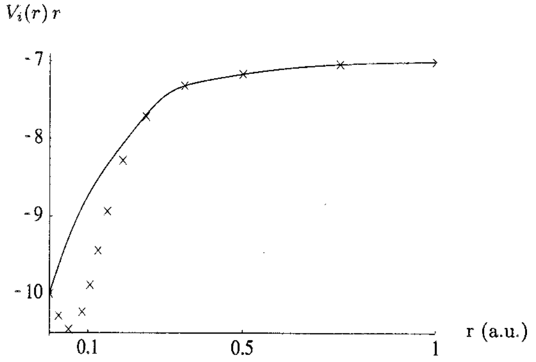


FIG. 5. Potential $V_i(r)$ for $\text{Ne}^{6+}$ times electron-nucleus distance $r$; $i=$KLI in full line and $i=$model in crosses.

$2p$ unchanged. This component was chosen as a Gaussian function centered at $10r = 0.763\,932$ a.u. in Eq. (2) (see also Fig. 5), because at this distance the radial density of $2s$ has a secondary maximum whereas it is small for $2p$. With this potential, $a = -0.275\,935$ and $b = 0.109\,424$ (for instance), we obtained $E^{(2)}_{V_{model}} - E_{V_{model}} = E_{CCSD(V_{model})} - E_{V_{model}} = -1.7237$ hartree. This correlation energy is of the order of magnitude ten times of that obtained with HF or KLI ($-178.8$ and $-179.8$ mhartree, respectively) as we used at no time the variational principle for generating $V_{model}$. However, it is still about 1% of the total energy $-110.2890$ hartree (the exact [22] being $-110.2910$ hartree). As expected, the HOMO-LUMO gap for $V_{model}$ (1124 mhartree) is greater than KLI's (658 mhartree) and lower than HF's (1713 mhartree). Too strong correlation energies are thus not systematically obtained at second-order perturbation theory, provided that local potentials are used. Moreover, as $b$ is increased (the $2s$ is lowered and the gap enlarged), it will become too weak.

In approximations of type (b), the equations were found strictly potential independent to first order in $Z$, as for the exact correlation energy (cf. Appendix B). To be specific, in the Be and Mg series, as there is only one valence pair to be excited, the coupled-cluster approximation is equivalent to a simple and double CI, which gives precisely the exact $Z$-linear coefficient of the correlation energy. For the Ar series (eight valence electrons), we should obtain a difference to first order in $Z$ between the exact and the CCSD correlation energies due to the presence of higher than double excitations in the hydrogenic spectrum.

## IV. CONCLUSIONS AND OUTLOOKS

Correlated calculations using different potentials (HF, XLDA, KLI, KS) and systems (He, Be, Ne, Mg, Ar series) were compared quantitatively in the first part (Sec. II) and qualitatively (at large $Z$) in the second part (Sec. III) of the paper.

*a. System-specific point of view*. We found from the above two approaches that approximate correlation energies in highly charged closed-shell ions could be partitioned into a system-specific contribution (linear with $Z$) in case of near degeneracy and a mostly $Z$-independent contribution. Then, we can imagine the latter nonspecific part to be given approximately by a universal model Hamiltonian, the homogeneous electron gas for argument's sake. Another possible continuation of the preceding analysis would be the extension to molecules. However, in that case the partition is not so obvious: in heteronuclear molecules, several $Z$ come into play, and even in homonuclear molecules, we have the problem that the degeneracy degree of the model system would be affected by internuclear distances.

*b. Reference-specific point of view*. Changing the potential from HF to XLDA, KLI, or KS had qualitatively no effect on the behavior of the correlation energy within a series. Quantitatively, it was of weak effect on the CCSD total energy in regard of the accuracy of the method itself. This result supports, in particular, that the terms not included in CCSD, such as triple excitations (which are needed in complex polyelectronic atoms and molecules for attaining chemical accuracy), cannot be avoided by a judicious choice for the potential. By contrast, the second-order perturbation theory was found very sensitive to the model Hamiltonian. As a rule, the local potentials studied here yielded very bad second-order energies whilst the HF-based results remained relatively good approximations to the exact energies. In a forthcoming paper, it will be shown that significant dependence upon the potential is obtained in both perturbation theory and coupled clusters when the active space is limited to a small energy band. In that case, some potentials will prove more suitable for describing the system-specific contribution mentioned above in Sec. IV A. For the present, we also pointed out the notably faster convergence of CCSD with local potentials. In particular, the Be atom converged in a very few iterations. The reasons why such a fast convergence was obtained in CCSD when some local potentials are used should be clarified and exploited. Some approximations to the coupled-cluster equations may also be conceivable, by inspecting more carefully the behavior of local potentials in the first iterations. Another possible continuation to this work would be to try the KLI orbitals in multireference calculations, and see how they behave with respect to the intruder-state problem for the ground state of Be [33].

## ACKNOWLEDGMENTS

The authors want to thank F. Colonna and C. Umrigar for communication of the Kohn-Sham potentials; E. Engel, K. Jankowski, R. J. Bartlett, and G. E. Scuseria are gratefully acknowledged for helpful discussions on the use of local potentials in coupled-cluster calculations.

## APPENDIX A: THE UNPERTURBED HAMILTONIAN WITH REFERENCE TO THE *N*-HYDROGENIC SYSTEM UNDER *Z* EXPANSION

The Hamiltonian $\mathcal{H}$ of the system with $N$ electrons and nuclear charge $Z$ is partitioned as

$$\mathcal{H} = \mathcal{H}_m + \mathcal{V}, \tag{A1}$$

where $\mathcal{H}_m$ is the model Hamiltonian

$$\mathcal{H}_m = \sum_{i=1}^{N} \left[ -\frac{1}{2}\nabla_i^2 + V_m(r_i) \right], \tag{A2}$$

and the spherically symmetric potential $V_m$ acting on the $i$th particle of radial coordinate $r_i$ stands either for $V_{HF}$ or $V_{KLI}$. The solutions of the independent-particles equation (A2) are the Slater determinants $\Phi_{I,m}$ constructed from $N$ orbitals $\phi_{i,m}(\mathbf{r})$ of energy $\epsilon_{i,m}$ and satisfying the one-particle equation

$$\left[ -\frac{1}{2}\nabla^2 + V_m(r) \right] \phi_{i,m}(\mathbf{r}) = \epsilon_{i,m}\phi_{i,m}(\mathbf{r}). \tag{A3}$$

Among all the $\Phi_{I,m}$'s, the ground-state $\Phi_{0,m}$ corresponding to the $N$ orbitals with lowest energy is chosen as a starting point for the perturbation. In case of degeneracy, we can always choose one of the degenerate determinants arbitrarily to be $\Phi_{0,m}$. In order to make explicit the $Z$ dependence at large $Z$ in Eq. (A1) and its solutions, we follow the treatment of Linderberg and Shull [21] and change to modified Hartree units. $\mathcal{H}$ is transformed to $\tilde{\mathcal{H}}$,

$$\tilde{\mathcal{H}}=\sum_{i=1}^{N}\left[-\frac{1}{2}\tilde{\nabla}_i^2-\frac{1}{\tilde{r}_i}+\frac{1}{2}\sum_{j=1}^{N}\frac{1}{Z\widetilde{r_{ij}}}\right], \tag{A4}$$

and similarly for $\mathcal{H}_m$,

$$\tilde{\mathcal{H}}_m=\sum_{i=1}^{N}\left[-\frac{1}{2}\tilde{\nabla}_i^2+\tilde{V}_m(\tilde{r}_i)\right], \tag{A5}$$

with

$$\tilde{V}_m(\tilde{r})=-\frac{1}{\tilde{r}}+\frac{1}{Z}\tilde{V}_m^{(1)}(\tilde{r})+\mathcal{O}\left(\frac{1}{Z^2}\right). \tag{A6}$$

In Eq. (A6), the first term $-1/r$ arises from the nucleus-electron attraction only whereas $\tilde{V}_m^{(1)}(\tilde{r})$ is the $1/Z$-order component of the potential modeling electron-electron repulsions. The expressions for $\tilde{V}_m^{(1)}(\tilde{r})$ are detailed in Appendix C when $V_m=V_{HF}$ or $V_{KLI}$. Now, at large $Z$, $\tilde{\epsilon}_{i,m}$ and $\tilde{\phi}_{i,m}(\tilde{\mathbf{r}})$ can be developed around their infinite-$Z$ hydrogenic values $\tilde{\epsilon}_{i,H}$ and $\tilde{\phi}_{i,H}(\tilde{\mathbf{r}})$, respectively, which are solutions of the $N$-hydrogenic Hamiltonian

$$\tilde{\mathcal{H}}_H=\sum_{i=1}^{N}\left[-\frac{1}{2}\tilde{\nabla}_i^2-\frac{1}{\tilde{r}_i}\right]. \tag{A7}$$

We obtain

$$\tilde{\epsilon}_{i,m}=\tilde{\epsilon}_{i,H}+\frac{1}{Z}\tilde{\epsilon}_{i,m}^{(1)}+\mathcal{O}\left(\frac{1}{Z^2}\right), \tag{A8}$$

$$\tilde{\phi}_{i,m}(\tilde{\mathbf{r}})=\tilde{\phi}_{i,H}(\tilde{\mathbf{r}})+\frac{1}{Z}\tilde{\phi}_{i,m}^{(1)}(\tilde{\mathbf{r}})+\mathcal{O}\left(\frac{1}{Z^2}\right), \tag{A9}$$

where $\tilde{\epsilon}_{i,m}^{(1)}$ and $\tilde{\phi}_{i,m}^{(1)}(\tilde{\mathbf{r}})$ are $Z$-independent first-order corrections given by nondegenerate perturbation theory applied to Eq. (A3) turned to modified Hartree units [$\tilde{\phi}_{i,m}^{(1)}(\tilde{\mathbf{r}})$ is not normalized]. Then, the $\tilde{\Phi}_{I,m}$'s are constructed from $N$ orbitals $\tilde{\phi}_{i,m}(\tilde{\mathbf{r}})$ expanded as in Eq. (A9); $Z$ ordering of the corresponding expression leads to

$$\tilde{\Phi}_{I,m}=\tilde{\Phi}_{I,H}+\frac{1}{Z}\,\tilde{\Phi}_{I,m}^{(1)}+\mathcal{O}\left(\frac{1}{Z^2}\right), \tag{A10}$$

where $\tilde{\Phi}_{I,H}$ and $\tilde{\Phi}_{I,m}^{(1)}$ (linear combination of the determinants differing from $\tilde{\Phi}_{I,H}$ by one spin orbital exactly) are $Z$ independent. The eigenvalues associated with $\tilde{\Phi}_{I,m}$ are also expanded as

$$\tilde{E}_{I,m}=\tilde{E}_{I,H}+\frac{1}{Z}\,\tilde{E}_{I,m}^{(1)}+\mathcal{O}\left(\frac{1}{Z^2}\right), \tag{A11}$$

where $\tilde{E}_{I,H}$ and $\tilde{E}_{I,m}^{(1)}$ are $Z$ independent. By expanding the energy of the monodeterminantal ground-state wave function $\tilde{\Phi}_{0,m}$ to order $1/Z$, we find

$$\tilde{E}_0=\langle\tilde{\Phi}_{0,m}|\tilde{H}|\tilde{\Phi}_{0,m}\rangle=\langle\tilde{\Phi}_{0,H}|\tilde{H}|\tilde{\Phi}_{0,H}\rangle+\mathcal{O}\left(\frac{1}{Z^2}\right), \tag{A12}$$

i.e.,

$$\tilde{E}_0=\tilde{E}_{0,H}+\frac{1}{Z}\tilde{E}_0^{(1)}+\mathcal{O}\left(\frac{1}{Z^2}\right), \tag{A13}$$

where

$$\tilde{E}_{0,H}=\langle\tilde{\Phi}_{0,H}|\tilde{\mathcal{H}}_H|\tilde{\Phi}_{0,H}\rangle$$

and

$$\tilde{E}_0^{(1)}=\langle\tilde{\Phi}_{0,H}|\Sigma_{i<j}(1/\tilde{r}_{ij})|\tilde{\Phi}_{0,H}\rangle.$$

(The numerical results for $\tilde{E}_{0,H}$ and $\tilde{E}_0^{(1)}$ in the He, Be, Ne, Mg, and Ar series are reported in Table IV.) Obviously, the choice for $\tilde{\mathcal{H}}_m$ is immaterial in $\tilde{E}_0$ to order $1/Z$ [see Eq. (A12)]. Thus, the correlation energies obtained with different potentials (for instance, $V=V_{HF}$, $V_{KLI}$) obey the definition $\tilde{E}_c=\tilde{E}-\tilde{E}_0$, unique to order $1/Z$ [the unique reference being the $N$-hydrogenic system, cf. Eq. (A7)]. As a consequence, the correlation energies $\tilde{E}_c$ can be compared directly to order $1/Z$, when $V_m$ is varied and the total energies $\tilde{E}$ are submitted to different approximations.

## APPENDIX B: THE CORRELATION ENERGY $\tilde{E}_C$ TO ORDER 1/$Z$ IN APPROXIMATE METHODS

We ask now the question of the dependence of approximate $\tilde{E}_c$ on the basis of determinants $\tilde{\Phi}_{I,m}$, eigenfunctions of the one-particle model Hamiltonians $\tilde{\mathcal{H}}_m$ (such as, e.g., HF, KLI). The Hamiltonians considered always give at zeroth order in $Z$ the same operator as the real Hamiltonian $\tilde{\mathcal{H}}$ [the $N$-hydrogenic Hamiltonian $\tilde{\mathcal{H}}_H$, cf. Eq. (A7)]:

$\tilde{\mathcal{H}}_m^{(0)}=\tilde{\mathcal{H}}^{(0)}=\tilde{\mathcal{H}}_H$. Thus, the correlation energy has no zeroth-order component. The first order in $1/Z$ is necessarily different, as $\tilde{\mathcal{H}}-\tilde{\mathcal{H}}^{(0)}$ contains a two-body operator, while $\tilde{\mathcal{H}}_m=\tilde{\mathcal{H}}_H+1/Z\ \ \tilde{\mathcal{H}}_m^{(1)}+\mathcal{O}(1/Z^2)$ is a one-body operator. The exact energy does not depend, of course, on the choice of the basis of the $\tilde{\Phi}_{I,m}$ (and thus on the choice of $\tilde{\mathcal{H}}_m$). However, approximate correlation energies can depend on $\tilde{\mathcal{H}}_m$. For example, consider the second-order perturbation theory:

$$\tilde{E}_{0,m}^{(2)}-\tilde{E}_0=\sum_{I\neq 0}\frac{|\langle\tilde{\Phi}_{0,m}|\tilde{\mathcal{H}}|\tilde{\Phi}_{I,m}\rangle|^2}{\tilde{E}_{0,m}-\tilde{E}_{I,m}}, \tag{B1}$$

where $\tilde{\Phi}_{I,m}$ differs from $\tilde{\Phi}_{0,m}$ by one or two excitations. To order $1/Z$,

$$\begin{aligned}\langle\tilde{\Phi}_{0,m}|\tilde{H}|\tilde{\Phi}_{I,m}\rangle &= \left\langle \tilde{\Phi}_{0,H}+\frac{1}{Z}\,\tilde{\Phi}^{(1)}_{0,m}\right|\tilde{H}_H+\frac{1}{Z}\sum_{i<j}^{N}\frac{1}{\tilde{r}_{ij}}\left|\tilde{\Phi}_{I,H}\right.\\ &\quad \left.+\frac{1}{Z}\tilde{\Phi}^{(1)}_{I,m}\right\rangle+\mathcal{O}\left(\frac{1}{Z^2}\right)\\ &=\frac{1}{Z}\Bigg(\langle\tilde{\Phi}^{(1)}_{0,m}|\tilde{\Phi}_{I,H}\rangle\tilde{E}_{I,H}+\langle\tilde{\Phi}_{0,H}|\tilde{\Phi}^{(1)}_{I,m}\rangle\tilde{E}_{0,H}\\ &\quad+\left\langle\tilde{\Phi}_{0,H}\left|\sum_{i<j}^{N}\frac{1}{\tilde{r}_{ij}}\right|\tilde{\Phi}_{I,H}\right\rangle\Bigg)\\ &\quad+\mathcal{O}\left(\frac{1}{Z^2}\right)\quad \text{for}\quad I\\ &\neq 0 \end{aligned}\tag{B2}$$

and

$$\tilde{E}_{0,m}-\tilde{E}_{I,m}=\tilde{E}_{0,H}-\tilde{E}_{I,H}+\frac{1}{Z}(\tilde{E}^{(1)}_{0,m}-\tilde{E}^{(1)}_{I,m})+\mathcal{O}\left(\frac{1}{Z^2}\right).\tag{B3}$$

If the states $I$ and 0 are not degenerate, $\tilde{E}_{0,m}-\tilde{E}_{I,m}$ is a constant independent of $Z$, and $|\langle\tilde{\Phi}_{0,m}|\tilde{H}|\tilde{\Phi}_{I,m}\rangle|^2/(\tilde{E}_{0,m}-\tilde{E}_{I,m})$ is proportional to $1/Z^2$; this will not be considered now. If the state $I$ is degenerate with the state 0, $\langle\tilde{\Phi}_{0,m}|\tilde{H}|\tilde{\Phi}_{I,m}\rangle$ can be nonzero but $\tilde{E}_{0,m}-\tilde{E}_{I,m}=1/Z(\tilde{E}^{(1)}_{0,m}-\tilde{E}^{(1)}_{I,m})+\mathcal{O}(1/Z^2)$ and thus $|\langle\tilde{\Phi}_{0,m}|\tilde{H}|\tilde{\Phi}_{I,m}\rangle|^2/(\tilde{E}_{0,m}-\tilde{E}_{I,m})$, being proportional to $1/Z$, has to be kept. We will say that only intravalence excitations can contribute to order $1/Z$ to the correlation energy. Thus, via the energy denominators, the first-order correlation energy $\tilde{E}^{(2)}_{0,m}-\tilde{E}_0$ can depend on the choice of $\tilde{\mathcal{H}}_m$. We mention also at this stage that $I$ can in fact only designate double excitations $(D)$. Actually, we showed in Appendix D that the only nonzero monoexcitations contributing to the correlation energy are those involving orbitals of the same angular symmetry. As a symmetry occurs only once in the valence shell, they are exactly zero to order $1/Z$ (even for potentials that do not satisfy exactly Brillouin's theorem as KLI).

There is a whole class of approximations, such as CI using only singly and doubly excited states, CCSD, etc., where the energy and the expansion coefficients are obtained via equations of the type

$$\sum_J \langle\tilde{\Phi}_{I,m}|\tilde{\mathcal{H}}-\tilde{E}_0|\tilde{\Phi}_{J,m}\rangle\tilde{c}_{J,m}=X_I,\tag{B4}$$

where $\tilde{\Phi}_{J,m}$ belongs now to a subset of determinants and $X_I$ may be zero or may be a function of terms of the type $\langle\tilde{\Phi}_{0,m}|\tilde{\mathcal{H}}|\tilde{\Phi}_{L,m}\rangle$ $(0\neq L)$ multiplied by expansion coefficients $\tilde{c}_{L,m}$ and $\tilde{c}_{I,m}$ (this is often done to guarantee size consistency). $Z$ expansion of the above equations (B4) is obtained by replacement of $\tilde{\mathcal{H}}$ with Eq. (A4), $\tilde{\Phi}_{I,m}$ with Eq. (A10), $\tilde{E}_0$ with Eq. (A13), and $\tilde{c}_{J,m}$ with $\tilde{c}_{J,H}+1/Z\tilde{c}^{(1)}_{J,m}+\mathcal{O}(1/Z^2)$, $\tilde{c}_{J,H}$ and $\tilde{c}^{(1)}_{J,m}$ being $Z$ independent. Zeroth order then yields $(\tilde{E}_{I,H}-\tilde{E}_{0,H})\tilde{c}_{I,H}=0$, meaning that nonzero $\tilde{c}_{I,H}$ correspond to those $\tilde{\Phi}_{I,H}$ that are degenerate with $\tilde{\Phi}_{0,H}$. We are interested now in analyzing the first-order terms. They may arise either from first-order matrix elements $\langle\tilde{\Phi}_{I,m}|\tilde{\mathcal{H}}|\tilde{\Phi}_{J,m}\rangle^{(1)}$ multiplied by zeroth-order coefficients $\tilde{c}_{J,H}$,

$$\begin{aligned}&\langle\tilde{\Phi}_{I,m}|\tilde{\mathcal{H}}|\tilde{\Phi}_{J,m}\rangle^{(1)}\tilde{c}_{J,H}\\ &\quad=\Bigg(\langle\tilde{\Phi}^{(1)}_{I,m}|\tilde{\Phi}_{J,H}\rangle\tilde{E}_{J,H}+\langle\tilde{\Phi}_{I,H}|\tilde{\Phi}^{(1)}_{J,m}\rangle\tilde{E}_{I,H}\\ &\qquad+\left\langle\tilde{\Phi}_{I,H}\left|\sum_{i<j}^{N}\frac{1}{\tilde{r}_{ij}}\right|\tilde{\Phi}_{J,H}\right\rangle\Bigg)\tilde{c}_{J,H}\end{aligned}\tag{B5}$$

or zeroth-order matrix elements $\langle\tilde{\Phi}_{I,m}|\tilde{\mathcal{H}}|\tilde{\Phi}_{J,m}\rangle^{(0)}$ multiplied by first-order coefficients $\tilde{c}^{(1)}_{J,m}$,

$$\langle\tilde{\Phi}_{I,m}|\tilde{\mathcal{H}}|\tilde{\Phi}_{J,m}\rangle^{(0)}\tilde{c}^{(1)}_{J,m}=\tilde{E}_{I,H}\delta_{I,J}\tilde{c}^{(1)}_{J,m}.\tag{B6}$$

In particular, the first-order correlation energy involves both terms developed in Eqs. (B5) and (B6), with $I=0$ and $J\neq 0$. In that case, Eq. (B5) is nonzero only if $\tilde{c}_{J,H}\neq 0$, i.e., $J$ belongs to the degenerate set. It follows that $\tilde{E}_{J,H}=\tilde{E}_{0,H}$ in Eq. (B5), canceling the dependence upon the potential through the first-order normalization condition $\langle\tilde{\Phi}^{(1)}_{0,m}|\tilde{\Phi}_{J,H}\rangle+\langle\tilde{\Phi}_{0,H}|\tilde{\Phi}^{(1)}_{J,m}\rangle=0$. Equation (B6) brings no contribution as $J\neq 0$. In brief, we showed that first-order $\tilde{E}_c$ is determined only in terms of zeroth-order coefficients $\tilde{c}_{I,H}$, with $I$ in the degenerate set. For such $I$'s, Eq. (B5) is nonzero only if $J$ belongs to the degenerate set. Then, Eq. (B5) reduces again to its last term, independent of the potential, due to the normalization condition $\langle\tilde{\Phi}^{(1)}_{I,m}|\tilde{\Phi}_{J,H}\rangle+\langle\tilde{\Phi}_{I,H}|\tilde{\Phi}^{(1)}_{J,m}\rangle=0$. Equation (B6) will never bring a contribution as either $I\neq J$ and it is zero, or $I=J$ (in the degenerate set) and Eq. (B6) occurs in Eq. (B4) as $\langle\tilde{\Phi}_{I,H}|\tilde{\mathcal{H}}_H-\tilde{E}_{0,H}|\tilde{\Phi}_{I,H}\rangle\tilde{c}^{(1)}_{I,m}=0$. We have thus shown that there is no dependence on $\tilde{\mathcal{H}}_m$ when determining $\tilde{E}_c$ with Eq. (B4) to first order in $1/Z$. Note that such was trivially also the case for full CI.

## APPENDIX C: EXPRESSIONS FOR THE FIRST-ORDER POTENTIALS $V^{(1)}_{HF}$ AND $V^{(1)}_{KLI}$

Let us define $\tilde{n}_a(\tilde{\mathbf{r}})$ and $\tilde{n}_{a,H}(\tilde{\mathbf{r}})$ as the densities of the $a$th orbitals $\phi_a(\tilde{\mathbf{r}})$ and $\phi_{a,H}(\tilde{\mathbf{r}})$, respectively: $\tilde{n}_a(\tilde{\mathbf{r}})=\phi^{\star}_a(\tilde{\mathbf{r}})\phi_a(\tilde{\mathbf{r}})$ and $\tilde{n}_{a,H}(\tilde{\mathbf{r}})=\phi^{\star}_{a,H}(\tilde{\mathbf{r}})\phi_{a,H}(\tilde{\mathbf{r}})$. We have the relation $\tilde{n}_a(\tilde{\mathbf{r}})=\tilde{n}_{a,H}(\tilde{\mathbf{r}})+\mathcal{O}(1/Z^2)$. The corresponding total spin densities are thus $\tilde{n}(\tilde{r})=\Sigma^{N/2}_{a\in\mathrm{occ}}\tilde{n}_a(\tilde{\mathbf{r}})$; $\tilde{n}_H(\tilde{r})=\Sigma^{N/2}_{a\in\mathrm{occ}}\tilde{n}_{a,H}(\tilde{\mathbf{r}})$ and we have $\tilde{n}(\tilde{r})=\tilde{n}_H(\tilde{r})+\mathcal{O}(1/Z^2)$.

### 1. $V_h^{(1)}$

When $V=V_{HF}$ or $V_{KLI}$, the electron-electron repulsion potential contains a Coulombian part of the Hartree type:

$$\tilde{V}_h(\tilde{r})=\frac{1}{Z}\int\frac{\tilde{n}(r')}{|\tilde{\mathbf{r}}-\tilde{\mathbf{r}}'|}d\mathbf{r}'=\frac{1}{Z}\int\frac{\tilde{n}_H(r')}{|\tilde{\mathbf{r}}-\tilde{\mathbf{r}}'|}d\mathbf{r}'+\mathcal{O}\left(\frac{1}{Z^2}\right). \tag{C1}$$

The part of the potential modeling exchange is reference specific, and we specify its expression below when $V=V_{HF}$ or $V_{KLI}$.

### 2. $V_{x,HF}^{(1)}$

In the Hartree-Fock approximation, every $i$th orbital has its own exchange potential $\tilde{V}_{x,i,HF}(\tilde{r})$:

$$\tilde{V}_{x,i,HF}(\tilde{r})=\tilde{v}_i(\tilde{r})=\tilde{v}_{i,H}(\tilde{r})+\mathcal{O}\left(\frac{1}{Z^2}\right), \tag{C2}$$

where

$$\begin{aligned}\tilde{v}_i(\tilde{r})&=-\frac{1}{Z}\sum_{a\in\mathrm{occ}}^{N/2}\frac{\tilde{\phi}_a(\tilde{\mathbf{r}})}{\tilde{\phi}_i(\tilde{\mathbf{r}})}\int d\mathbf{r}'\frac{\tilde{\phi}_a^{\star}(\widetilde{\mathbf{r}'})\tilde{\phi}_i(\widetilde{\mathbf{r}'})}{|\tilde{\mathbf{r}}-\tilde{\mathbf{r}}'|}\\&=-\frac{1}{Z}\sum_{a\in\mathrm{occ}}^{N/2}\frac{\tilde{\phi}_{a,H}(\tilde{\mathbf{r}})}{\tilde{\phi}_{i,H}(\tilde{\mathbf{r}})}\int d\mathbf{r}'\frac{\tilde{\phi}_{a,H}^{\star}(\widetilde{\mathbf{r}'})\tilde{\phi}_{i,H}(\widetilde{\mathbf{r}'})}{|\tilde{\mathbf{r}}-\tilde{\mathbf{r}}'|}\\&\quad+\mathcal{O}\left(\frac{1}{Z^2}\right)\end{aligned} \tag{C3}$$

and

$$\tilde{v}_{i,H}(\tilde{r})=-\frac{1}{Z}\sum_{a\in\mathrm{occ}}^{N/2}\frac{\tilde{\phi}_{a,H}(\tilde{\mathbf{r}})}{\tilde{\phi}_{i,H}(\tilde{\mathbf{r}})}\int d\mathbf{r}'\frac{\tilde{\phi}_{a,H}^{\star}(\widetilde{\mathbf{r}'})\tilde{\phi}_{i,H}(\widetilde{\mathbf{r}'})}{|\tilde{\mathbf{r}}-\tilde{\mathbf{r}}'|}. \tag{C4}$$

### 3. $V_{x,KLI}^{(1)}$

In the KLI approximation, the exchange potential $\tilde{V}_{x,KLI}(\tilde{r})$ is an average of Hartree-Fock potentials over occupied orbital densities,

$$\tilde{V}_{x,KLI}(\tilde{r})=\sum_{b\in\mathrm{occ}}^{N/2}\frac{\tilde{n}_b(\tilde{r})}{\tilde{n}(\tilde{r})}(\tilde{v}_b(\tilde{r})+\tilde{c}_b) \tag{C5}$$

and the constants $\tilde{c}_b$ are

$$\tilde{c}_b=\begin{cases}\int(\tilde{V}_{x,KLI}(\tilde{r})-\tilde{v}_b(\tilde{r}))\tilde{n}_b(\tilde{r}) & \text{if } b\neq\mathrm{HOMO}\\ 0 & \text{otherwise,}\end{cases} \tag{C6}$$

where $\tilde{c}_b(b=\mathrm{HOMO})$ is chosen such that $\tilde{V}_{x,KLI}(\tilde{r})$ has the asymptotic behavior $-1/\tilde{r}$ at large $\tilde{r}$. For the Ne and Ar series (systems with more than two valence electrons), at infinite $Z$, there are rigorously several degenerate highest occupied orbitals with zero constants to guarantee the correct asymptotic behavior of the potential. However, as the $1/Z$ calculations are used here to compare with our complete calculations, we considered implicitly that the hydrogenic orbitals were filled as the full KLI orbitals for finite $Z$. As a consequence, for Ne series, only $\tilde{c}_{2p}=0$ and for Ar series only $\tilde{c}_{3p}=0$. With these conventions, the fitted full calculations coincide with the $1/Z$ expansion for the orbital energies to be used in Eq. (1).

## APPENDIX D: ANGULAR SELECTION RULE FOR SINGLE EXCITATIONS

Let $\Phi$ be any Slater determinant and $\Phi_a^r$ a monoexcited determinant constructed from $\Phi$ by substituting the virtual orbital $\phi_r$ for the occupied orbital $\phi_a$. In this section, we find the conditions for having $\langle\Phi|\mathcal{H}|\Phi_a^r\rangle=0$. According to the Slater rules, the monoelectronic part must be zero unless diagonal, i.e., $l_a=l_r$ and $m_a=m_r$. The bielectronic part splits into

$$\begin{aligned}\left\langle\Phi\left|\sum_{i<j}\frac{1}{r_{ij}}\right|\Phi_a^r\right\rangle&=\sum_b^{\mathrm{occ}}2\left\langle\phi_a\phi_b\left|\frac{1}{r_{12}}\right|\phi_r\phi_b\right\rangle\\&\quad-\left\langle\phi_a\phi_b\left|\frac{1}{r_{12}}\right|\phi_b\phi_r\right\rangle.\end{aligned} \tag{D1}$$

Let us manipulate the right-hand side of Eq. (D1) assuming that $a$ and $r$ are fixed and $1/r_{12}$ is expanded as a product of spherical harmonics $Y_{l_k}^{m_k}$. For the first term on the right-hand side, we considered only the sum over the subshells $m_b$, and found the proportionality relation

$$\begin{aligned}&\sum_{m_b}\langle\phi_a\phi_b|\phi_r\phi_b\rangle\\&\quad\propto\int\int d\Omega_1 d\Omega_2\sum_{m_b=-l_b}^{l_b}\sum_{k=0}^{\infty}\sum_{q=-k}^{k}\frac{4\pi}{2k+1}(Y_{l_a}^{m_a}{*}Y_{l_r}^{m_r}Y_k^q)\\&\quad\times(\Omega_1)(Y_{l_b}^{m_b}{*}Y_{l_b}^{m_b}Y_k^q{*})(\Omega_2)\end{aligned} \tag{D2}$$

$$\begin{aligned}&=\int\int d\Omega_1 d\Omega_2\sum_{k=0}^{\infty}\sum_{q=-k}^{k}\frac{2l_b+1}{2k+1}(Y_{l_a}^{m_a}{*}Y_{l_r}^{m_r}Y_k^q)\\&\quad\times(\Omega_1)Y_k^q{*}(\Omega_2)\end{aligned} \tag{D3}$$

$$=\int d\Omega_1(2l_b+1)(Y_{l_a}^{m_a}{*}Y_{l_r}^{m_r})(\Omega_1)\sqrt{4\pi}. \tag{D4}$$

To obtain Eq. (D3) from Eq. (D2), the normalization of the subshell $m_b$ $[\Sigma_{m_b=-l_b}^{l_b}(Y_{l_b}^{m_b\star}Y_{l_b}^{m_b})=(2l_b+1)/(4\pi)]$ has been used. To obtain Eq. (D4) from Eq. (D3) the integration over $\Omega_2$ has been done. The only nonzero result corresponds to an $s$ symmetry for $Y_k^q$, i.e. $k=q=0$. Now, focusing on the integral over $\Omega_1$, the only nonzero term is obtained for $Y_{l_a}^{m_a}=Y_{l_r}^{m_r}$, i.e., $l_a=l_r$ and $m_a=m_r$

We proceed similarly for the second term on the right-hand side of Eq. (D1):

$$\sum_{m_b} \langle \phi_a \phi_b | \phi_b \phi_r \rangle$$

$$\propto \int \int d\Omega_1 d\Omega_2 \sum_{m_b=-l_b}^{l_b} \sum_{k=0}^{\infty} \sum_{q=-k}^{k} \frac{4\pi}{2k+1} (Y_{l_a}^{m_a}{*} Y_{l_b}^{m_b} Y_k^q) \times (\Omega_1)(Y_{l_b}^{m_b}{*} Y_{l_r}^{m_r} Y_k^q{*})(\Omega_2) \tag{D5}$$

$$= \sum_{m_b=-l_b}^{l_b} \sum_{k=0}^{\infty} \sum_{q=-k}^{k} \frac{4\pi}{2k+1} (-1)^q \sqrt{\frac{2l_b+1}{4\pi}} \times (-1)^{m_a} \sqrt{(2l_a+1)(2k+1)} \begin{pmatrix} l_a & l_b & k \\ -m_a & m_b & q \end{pmatrix} \times \begin{pmatrix} l_a & l_b & k \\ 0 & 0 & 0 \end{pmatrix} \sqrt{\frac{2l_r+1}{4\pi}} (-1)^{m_b} \sqrt{(2l_b+1)(2k+1)} \times \begin{pmatrix} l_b & l_r & k \\ -m_b & m_r & -q \end{pmatrix} \begin{pmatrix} l_b & l_r & k \\ 0 & 0 & 0 \end{pmatrix} \tag{D6}$$

$$= \sum_{k=0}^{\infty} (2l_b+1) \sqrt{2l_r+1} \sqrt{2l_a+1} \begin{pmatrix} l_a & l_b & k \\ 0 & 0 & 0 \end{pmatrix} \times \begin{pmatrix} l_b & l_r & k \\ 0 & 0 & 0 \end{pmatrix} \sum_{m_b=-l_b}^{l_b} \sum_{q=-k}^{k} \begin{pmatrix} l_a & l_b & k \\ -m_a & m_b & q \end{pmatrix} \times \begin{pmatrix} l_r & l_b & k \\ -m_r & m_b & q \end{pmatrix} (-1)^{2(l_b+l_r+k)} (-1)^{m_a+m_b+q} \tag{D7}$$

$$= \sum_{k=0}^{\infty} (2l_b+1) \begin{pmatrix} l_a & l_b & k \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_b & l_r & k \\ 0 & 0 & 0 \end{pmatrix} \times \delta(l_a-l_r)\, \delta(m_a-m_r) \tag{D8}$$

Equation (D6) comes from Eq. (D5) by expressing the integrals over three spherical harmonics in terms of the Wigner 3-$j$ symbols. For Eq. (D7) the terms are rearranged; then, we change the signs in a row and permutate two columns in the third 3-$j$ symbol. For Eq. (D8) the third 3-$j$ symbol vanishes unless $m_a = m_b + q$, i.e., $(-1)^{m_a+m_b+q} = 1$. The orthogonality relation of the 3-$j$ symbols over the subshells $m_b$ and $q$,

$$\sum_{m_b=-l_b}^{l_b} \sum_{q=-k}^{k} \begin{pmatrix} l_a & l_b & k \\ -m_a & m_b & q \end{pmatrix} \begin{pmatrix} l_r & l_b & k \\ -m_r & m_b & q \end{pmatrix} = (2l_a+1)^{-1} \delta(l_a-l_r)\, \delta(m_a-m_r),$$

has been used [ $\delta(x)=1$ if $x=0$, 0 otherwise]. Finally, the integral is nonzero only if $l_a = l_r$ and $m_a = m_r$. In a nutshell, we have the following proportionality relation true, independent of the orbitals:

$$\langle \Phi | H | \Phi_a^r \rangle \propto \delta(l_a - l_r)\, \delta(m_a - m_r). \tag{D9}$$

[1] H. Kelly, Phys. Rev. B **136**, B896 (1964).

[2] E.R. Davidson, J. Chem. Phys. **57**, 1999 (1972).

[3] A. Savin, C.J. Umrigar, and X. Gonze, Chem. Phys. Lett. **288**, 39 (1998).

[4] L. Fritsche, Phys. Rev. B **33**, 3976 (1986).

[5] A. Görling and M. Levy, Phys. Rev. B **47**, 13 105 (1993).

[6] J.D. Talman and W.F. Shadwick, Phys. Rev. A **14**, 36 (1976).

[7] E. Engel and R.M. Dreizler, J. Comput. Phys. **20**, 31 (1999).

[8] E. Engel, A. Höck, and R.M. Dreizler, Phys. Rev. A **61**, 032502 (2000).

[9] J. Krieger, Y. Li, and G. Iafrate, *Density Functional Theory*, edited by E. K. U. Gross and R. M. Dreizler (Plenum, New York, 1995).

[10] E. Engel, A. Höck, and R.M. Dreizler, Phys. Rev. A **62**, 042502 (2000).

[11] A. Görling, Phys. Rev. Lett. **83**, 5459 (1999).

[12] J. Krieger, J. Chen, G. Iafrate, and A. Savin, *Electron Correlation and Material Properties*, edited by A. Gonis, N. Kioussis and M. Ciftan (Kluwer/Plenum, New York, 1999).

[13] S. Shankar and P.T. Narasimhan, Phys. Rev. A **29**, 52 (1984).

[14] S. Shankar and P.T. Narasimhan, Phys. Rev. A **29**, 58 (1984).

[15] R. J. Bartlett, Symposium on Density Functional Theory and Applications, 1997 (unpublished).

[16] R. J. Bartlett and S. Ivanov (unpublished).

[17] C. Gutlé, A. Savin, J. Chen, and J.B. Krieger, Int. J. Quantum Chem. **75**, 885 (1999).

[18] C. Gutlë, A. Savin, and J. B. Krieger, *New Trends in Quantum Systems in Chemistry and Physics*, edited by J. Maruani *et al.* (Kluwer, Dordrecht, 2001).

[19] A.F. Bonetti, E. Engel, R.N. Schmid, and R.M. Dreizler, Phys. Rev. Lett. **86**, 2241 (2001).

[20] S. Salomonson, I. Lindgren, and A. Martenson, Phys. Scr. **21**, 351 (1980).

[21] J. Linderberg and H. Shull, J. Mol. Spectrosc. **5**, 1 (1960).

[22] S.J. Chakravorty, S.R. Gwaltney, E. Davidson, F.A. Parpia, and C.F. Fisher, Phys. Rev. A **47**, 3649 (1993).

[23] I. Lindgren and Chalmers Computer code HFJ8, 1985.

[24] Y. Li (unpublished).

[25] A. Savin, F. Colonna, and J.-M. Teuler, *Electronic Density Functional Theory*: *Recent Progress and New Directions*, edited by J. F. Dobson, G. Vignale, and M. P. Das (Plenum, New York, 1998).

[26] F. Colonna and A. Savin, J. Chem. Phys. **110**, 2828 (1999).

[27] C. Filippi, X. Gonze, and C. J. Umrigar, *Recent Developments and Applications of Density Functional Theory*, edited by J. M. Seminario (Elsevier, Amsterdam, 1996).

[28] E. Valderrama, E.V.L. Na, and J. Hinze, J. Chem. Phys. **110**, 2343 (1999).

[29] P.O. Löwdin, Adv. Chem. Phys. **2**, 207 (1959).

[30] M. Levy, Phys. Rev. A **43**, 4637 (1991).

[31] D.J. Thouless, Nucl. Phys. **21**, 255 (1960).

[32] J.-L. Heully and J.-P. Daudey, J. Chem. Phys. **88**, 1046 (1988).

[33] S. Salomnson, I. Lindgren, and A.-M. Martenson, Phys. Scr. **21**, 351 (1980).

[34] See EPAPS Document No. E-PLRAAN-65-135206 including (a) the following three tables, total energies in the Ne, Mg, and Ar series (Tables III (EPAPS), IV (EPAPS), and V (EPAPS) resp.); (b) two figures, convergence of CCSD in the Mg and Ar series [Fig. 5 (EPAPS) and 6 (EPAPS), respectively]. This document may be retrieved via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory/epaps/. See the EPAPS homepage for more information.

[35] Similar calculations were already presented for the KLI potential in the Be series [18] with typing errors: in Eq. (34), the constant of the KLI potential $-0.036\,0971/Z$ has to be replaced with $0.133\,292\,3/Z$. The resulting energy gap is thus $-0.167\,682/Z$ instead of $-0.123\,282/Z$ in Eq. (16) and the second-order $-0.015\,355\,9/Z$ instead of $-0.020\,887$ in Eq. (17).

[36] We call the system of $N$ noninteracting electrons in the field of a proton $N$ hydrogenic.

[37] Intravalence excitations are excitations from the valence shell to the valence shell. The valence shell is the shell including the highest occupied orbital. As we are here in the presence of the hydrogenic spectrum, notice that the valence shell is a subspace where all states are degenerate.