We analyze the Coulomb hole of Ne from highly-accurate CISD wave functions obtained from optimized even-tempered basis sets. Using a two-fold extrapolation procedure we obtain highly accurate results that recover 97% of the correlation energy. We confirm the existence of a shoulder in the short-range region of the Coulomb hole of the Ne atom, which is due to the correlation of the core electrons in the $K$ shell. The feature is not displayed in the Coulomb hole calculated with certain basis sets, such as the correlated-consistent basis set of Dunning, shedding some doubts on the quality of the description of the core electrons using these basis sets. The shoulder is due to an internal reorganization of the $K$ shell, where electrons are pushed towards the $K$-shell boundary. The short-range shoulder of the Coulomb hole is not exclusive to Ne atom and is also present in larger noble gases, their ions and noble-gas molecules, suggesting that this feature is characteristic of complete-shell species.

I. INTRODUCTION

Electron correlation is still a central problem in physics and chemistry. Its study often provides physical insights to develop new computational methods to tackle the electronic structure of molecules. The primitive description provided by the Hartree-Fock (HF) wave function is improved by consideration of different types of electron correlation, such as dynamic and nondynamic correlation, in the so-called post-HF methods or in methods that do not employ wave functions, such as the density and reduced-density matrix functional theories (DFT and RDMFT). The improvement of computational methods and tools, the correct choice of a computational protocol to address a given problem, and our understanding of the electron correlation pose, hinge on the development of appropriate descriptors of electron correlation. Lately, our efforts have concentrated in the direction, resulting in the development of simple electron correlation descriptors capable of separating dynamic and nondynamic correlation.

The Coulomb hole stands out among the classical descriptors that are used to study the electron correlation due to its conceptual simplicity and its connection with the electron-electron energy. The Coulomb hole provides a practical picture of how the electron correlation affects the interelectronic separation. Namely, it reflects the change of the electron-electron distance distribution upon the inclusion of electron correlation. From this quantity the correlation effects on the average interelectronic distance, its variance, and the electron-electron repulsion are easily assessed. The topological features of the Coulomb hole have also been studied, leading to some relevant conclusions about the nature of electron correlation. Some of us have also recently used the long-range part of the Coulomb hole to identify van der Waals interactions.

In this work, we analyze a certain feature of the Coulomb hole of the Ne atom that, thus far, has escaped the attention of quantum mechanics practitioners. In 1969, Bunge and coworkers identified a shoulder structure in the short-range part of the Coulomb hole of the Ne atom which was corroborated by Cioslowski and Liu thirty years later. Bunge attributed this peculiarity to the $K$-shell electrons, whereas Cioslowski did not comment on this feature. We have found that the shoulder is very sensible to the quality of the basis sets employed in the calculation, turning into a minimum or vanishing depending on the basis set. In order to confirm the presence of the shoulder we have performed CISD and FCI calculations employing large optimized even-tempered basis sets, which provide energy estimates that compare well with the most accurate values obtained by Bunge. Our results provide a thorough study on the origin of the shoulder, identifying the causes that are responsible for its presence. Finally, we prove that this feature is not exclusive to Ne atom, showing in other noble gases and like ions. These results suggest that the shoulder structure of the Coulomb hole might be connected with the complete-shell structure characteristic of these species.

II. METHODOLOGY

There are two different ways to define correlation holes: McWeeny’s and Coulson’s. The former is statistically motivated and it does not employ reference wave functions, whereas Coulson’s definition uses HF as the uncorrelated reference. In this work, we are concerned with Coulson’s definition, which is connected with an experimental observable. Coulson’s Coulomb hole is obtained from the difference between the exact and the HF in-
intracule densities. The radial intracule density provides a distribution of the electron-electron distances,

$$I(u) = \int \int dr_1 dr_2 n_2(r_1, r_2) \delta(u - r_{12}), \quad (1)$$

where $n_2(r_1, r_2)$ is the pair density and $r_{12}$ is the module of the intracule coordinate, $r_{12} = r_1 - r_2$. The X-ray scattering intensity is essentially determined by the Fourier-Bessel transform of the intracule pair density, and it is employed in the study of elastic and inelastic scattering of electrons. The total X-ray scattering intensity for short wavelengths is actually governed by the value of the intracule at the coalescence points, $I(0)$. The difference between the exact pair density and an uncorrelated reference, represents the change in electron pairing upon the introduction of electron correlation. Coulson’s Coulomb hole sets HF intracule pair density as the uncorrelated reference,

$$h_C(u) = I(u) - I_{HF}(u) \tag{2}$$

giving negative (positive) values for the interelectronic separations $u$ that are increased (decreased) upon the inclusion of correlation. The integration of $h_C(u)$ over $u$ gives zero.

The optimization of the basis sets employs an analogous procedure to the one developed elsewhere. This procedure has been successfully used to generate highly-accurate basis functions to test model systems and calculate a number of methods. First of all, a family of uncontracted basis sets consisting of spherical Gaussian primitives is constructed by selecting the optimized exponents that minimize the CISD energies (the coefficients that multiply the primitives are equal to 1 and do not enter the optimization procedure). From these values, the complete-basis set (CBS) estimate of Ne CISD energies are obtained by a two-fold extrapolation procedure.

The family of basis sets employs functions with exponents $\zeta_{L,N}$ that are even-tempered according to the expression

$$\zeta_{L,N}^k = \alpha_{L,N} [\beta_{L,N}]^{k-1}, \quad 1 \leq k \leq N. \tag{3}$$

Each basis set is characterized by the maximum angular momentum, $L$, and the number of basis functions for each function type, $N$. For instance, 6SP ($L = 1, N = 6$) basis set consists of six groups of functions containing one $S$ and three $P$ functions ($p_x, p_y$ and $p_z$) sharing the same exponent. The exponent assigned to each group is given by $k$ in Eq. (3) which runs from 1 to $N$. $\alpha_{L,N}$ and $\beta_{L,N}$ are, therefore, unique for each basis set and determined by minimization of the CISD energy of Ne with a simplex method (minimal accuracy $10^{-7}$ a.u.). The family includes basis sets with angular momentum between 0 and $L$ ($1 \leq L \leq 4$) and involve equal numbers $N$ ($6 \leq N \leq 16$) of spherical Gaussian primitives with exponents $\zeta_{L,N}$, giving rise to 44 different basis sets.

The computed energies $E_{L,N}$ have been extrapolated to the respective $N \rightarrow \infty$ limits $E_L$ by fitting the actual energy values for $N = 12, 13, 14, 15$ and 16 with the double-exponential expression

$$E_{L,N} = E_L + a_L e^{-\alpha_L N} + b_L e^{-\beta_L N}, \tag{4}$$

which generalizes the Dunning extrapolation. The resulting system of five non-linear equations has been solved analytically with Mathematica employing the Ramanujan algorithm.

In turn, the estimates $E_L$ have been extrapolated to the respective CBS limits $E_L$ by fitting the values of $E_L$ for $L = 2, 3,$ and 4 to the expression

$$E_L = E + \frac{B}{(L+1)^3}. \tag{5}$$

These extrapolations, $E_L$ and $E_L$, provide lower-energy estimates of the total energy that are not variational.

In the case of HF, the energy results are almost converged using only $S$ and $P$ basis functions. Therefore, we take the SP-energy limit as a good estimate of the CBS-extrapolated result. The numerical estimate is obtained from $N = 16, 17, 18, 19$ and 20 calculations applying the fitting of Eq. (5).

The full-configuration interaction (FCI) calculations have been carried out with a modified version of the FCI program of Knowles and Handy and the CISD calculations have been performed with Gaussian. The calculations of the second-order reduced density matrices (2-RDM) have been calculated from the FCI/CISD expansions coefficients using the in-house DMN code. The radial intracule density was computed with the in-house RHO2-OPS code which uses the algorithm proposed by Cioslowski and Liu.

### III. RESULTS

#### A. Benchmark data

Following the procedure described in the previous section we have obtained a CISD extrapolated energy of $-128.9254609$ a.u., which represents an energy lowering of $-0.0143834$ a.u. with respect to the best variational estimate, $E_{4,16}$ (see Table). These results compare well with the best non-relativistic FCI estimate available in the literature, $-128.937588$ a.u.

Our CISD SPDF-energy limit, $-128.8984284$ a.u., is in good agreement with the FCI value $-128.897 \pm 0.002$ a.u. calculated by Bunge. This and the other partial waves reported in Table are also in accord with the second-order correlation energies of Lindgren and Salomonson.

Our extrapolated HF energy, $-128.547100$ a.u., which also corresponds to the SP-energy limit, is in excellent agreement with the numerical HF results, $-128.547098$ a.u., reported elsewhere. Our best CISD estimate of the correlation energy is, therefore, $-0.378361$ a.u., which represents $97\%$ of the correlation energy of No. Our best variational estimate of the correlation energy, based on...
TABLE I. CISD energies (a.u.) for the basis set family developed in this work and the corresponding partial waves.

| N  | $E_{1,N}$      | $E_{2,N}$      | $E_{3,N}$      | $E_{4,N}$      |
|----|----------------|----------------|----------------|----------------|
| 5  | -128.7146757   | -127.9311638   | -127.9638254   | -127.9755176   |
| 6  | -128.3326841   | -128.4543077   | -128.4887366   | -128.5013557   |
| 7  | -128.5692718   | -128.6923709   | -128.7272631   | -128.7395973   |
| 8  | -128.6612028   | -128.7855792   | -128.8209903   | -128.835145    |
| 9  | -128.6987672   | -128.8280188   | -128.8598984   | -128.8725858   |
| 10 | -128.7176209   | -128.8433421   | -128.8794251   | -128.892251    |
| 11 | -128.7265782   | -128.8526131   | -128.8888885   | -128.9017858   |
| 12 | -128.7304973   | -128.8567898   | -128.8932237   | -128.9062091   |
| 13 | -128.7323966   | -128.8588808   | -128.8954410   | -128.9085010   |
| 14 | -128.7334758   | -128.8600836   | -128.8967326   | -128.9098489   |
| 15 | -128.7340477   | -128.8607425   | -128.8974582   | -128.9106198   |
| 16 | -128.7343430   | -128.8611063   | -128.8978764   | -128.9110766   |
| $\infty$ | -128.7346499   | -128.8615534   | -128.8984284   | -128.9117007   |

on the CISD/16SPDFG calculation (including 400 basis functions), recovers 93% of the correlation energy. Our calculations on the angular and the radial correlation indicators of Kutzelnigg show no qualitative improvement in the description of correlation beyond the 11SPDF basis set (see Figs. S1 and S2) and Bunge and coworkers report very small effects upon introduction of the triple and quadruple excitations (less than 0.01% change on the density). Therefore, we conclude that our CISD calculations provide a good description of electron correlation in Ne.

We have also explored the convergence of certain properties related to the Coulomb hole with the size of the basis set. Our results indicate that the average interelectronic distance and its variance are much more affected by the number of basis functions than by the inclusion of functions of large angular momentum. In this respect, the use of 9SP basis functions provides a reasonable description of these indicators (see Figs. S3 and S4). For this reason, we have chosen the CISD/9SP wave function to provide a qualitative explanation of the Coulomb hole in Ne atom. In some selected cases, analysis with larger basis sets have been performed to confirm our conclusions.

B. The Coulomb hole of the Ne atom

In his seminal paper, Carlos Bunge reported a small shoulder of the Coulomb hole of Ne that he attributed to the correlation of K-shell electrons. This calculation was based on a FCI wave function that yield an electronic energy of −128.8602 a.u. and, thus, only retrieved 85% of the correlation energy. Thirty years later, Cioslowski and Liu confirmed this result using 2-RDMs obtained from energy derivatives of MP2 calculations with a non-optimized even-tempered basis set of 50 functions (20×10p). We have tried to reproduce the results of Bunge and Cioslowski and have encountered a major difficulty choosing the appropriate basis set. We have performed over hundred CISD calculations (and some FCI calculations as well) using different basis with and without the frozen core approximation, finding that the shoulder is only reproduced in about half of the cases (see Tables S1 and S2). No frozen-core calculation could reproduce the shoulder structure regardless the size of the basis set, supporting the idea that this feature, if real, is a result of the correlation of the core electrons. The basis set families show similar results among its members. People’s 6-311G and larger basis of this family as well as the first family of basis sets developed by Dunning (nZ) display the shoulder structure. Conversely, the family of correlated-consistent basis sets of Dunning (cc-pVnZ) and the series of basis sets of Petersson cannot reproduce the shoulder structure (see Fig. 1 for some examples).

In order to solve this controversy, we have built a series of even-tempered basis sets following the procedure described above. For all these basis sets, regardless the size, the shoulder structure shows at ca. 0.1 Å (see Fig. 2). For small basis sets, including only S and P functions, the shoulder is actually a minimum, in accord with the results presented by Cioslowski and Liu that also employed only S and P functions. The shoulder structure, as reported by Bunge and Cioslowski shows using S, P and D functions. Augmenting with F functions does not produce a large change, and the addition of G functions barely changes the Coulomb hole, thus suggesting that the presence of the shoulder is not due to a basis set completeness problem (see Fig. 2). The role of core orbitals is evident because the corresponding frozen-core CISD (fc-CISD) calculations do not show any shoulder structure (see Fig. S5 in the Supporting Information).
hole structure (see HF+E in Fig. 4) that is responsible for
of double excitations from the core orbitals gives rise to a
configurations in retrieving the shoulder. The inclusion
and, therefore, should reflect the importance of certain
Unlike the previous CISD expansions, these ones only
configurations involving excitations from the 1s
orbital shows that
CISD expansion calculated with the 9SP basis set. In
Fig. 3 we have plotted the Coulomb hole generated with
the preferred virtual orbitals are 4s, 5s, 5p, and 6p.
After removal and addition of these configurations, the
expansion coefficients have been rescaled to attain the nor-
malization of the wave function.
the shoulder structure of the complete CISD expansion.
From this plot is also evident that double excitations and
particularly those involving 4s, 5s, 5p and 6p are mostly
responsible for the shoulder structure.
Thus far, we have firmly established the presence of the
shoulder in the Coulomb hole of Ne, which is
due to the electron correlation of core electrons. In
the following, we will analyze how the correlation
affects the electronic structure of Ne and the particular
role that the core electrons play in this context using
the CISD/16SP wave function. First of all, we will
consider the shell-structure of Ne. There has been some
controversy in the literature concerning the descriptor
that should be employed to identify the shell structure
and shell numbers in atoms57–59 in our opinion, the
one-electron potential (OEP) of Kohout being the most
robust suggestion made thus far.44 According to the
OEP, we find that the radius of the K shell does not
change upon inclusion of electron correlation effects
($r_K = 0.138\text{Å}$) and the K-shell number only increases
3 \times 10^{-3} \text{ electrons due to correlation ($n_{HF}^K = 2.0019$ e.)}
Therefore, according to the shell structure determined
by the OEP, we conclude that electron correlation does
not cause an expansion or contraction of the K shell,
but a small reorganization within the K shell, pushing
some electron density towards the K-shell boundary

FIG. 2. The CISD Coulomb hole of Ne for some even-
tempered basis sets.

C. The origin of the shoulder

In this section we analyze the reasons for the existence
of the shoulder in the Coulomb hole of Ne. We already
know that the correlation of core electrons is responsi-
ble for it. Let us now consider the importance of differ-
ent configurations by removing some of them from the
CISD expansion calculated with the 9SP basis set. In
Fig. 3 we have deleted various excitations from the core orbital
(1s). The CISD expansion in which we have removed
all the excitations from the core orbital except the single
excitations (CISD(nc)+A in Fig. 3) produces a Coulomb
hole that is virtually identical to the fc-CISD one. The
double excitations involving only one electron in 1s² pro-
give likewise a Coulomb hole qualitatively similar to the
fc-CISD wave function (CISD(nc)+B). Among the dou-
ble excitations the most important ones are those excited
simultaneously both 1s² electrons as evinced from the
shoulder structure of the Coulomb hole of the CISD
wave function where only these excitations from the core
orbital are retained (CISD(nc)+C). A detailed analysis
of the double excitations from the 1s orbital shows that
the preferred virtual orbitals are 4s, 5s, 5p, and 6p (see
CISD(nc)+D Coulomb hole in Fig. 3). These results have
been qualitatively confirmed with the CISD/16SPDFG
wave function (see Fig. S9 in the Supporting Informa-
Fig. 4 plots the Coulomb hole for CISD expansions
that only include the HF configuration and some chosen
configurations involving excitations from the 1s orbital.
Unlike the previous CISD expansions, these ones only
include correlation effects due to the core electrons in Ne
and, therefore, should reflect the importance of certain
configurations in retrieving the shoulder. The inclusion
of double excitations from the core orbitals gives rise to a
hole structure (see HF+E in Fig. 4) that is responsible for

FIG. 3. The CISD/9SP Coulomb hole in terms of several ex-
...
FIG. 4. The CISD/9SP Coulomb hole in terms of several expansions. The groups of configurations allowed involve excitations from the core orbitals to some particular virtual orbitals (see the caption of Fig. 3 for C and D). The E group includes configurations involving double excitations from 1s to all virtual orbitals.

FIG. 5. The dynamic part ($h_D$) and the total ($h_T$) Coulomb hole of Ne at the CISD/16SPDFG level of theory.

D. Other noble-gas-like atoms, ions and molecules.

There have been various studies of the Coulomb hole structure of atoms and molecules, but, to our knowledge, only Ne atom and two isoelectronic ions, Na$^+$ and F$^-$, present a Coulomb hole with a shoulder at short distances. It is well known that the Coulomb hole of He does not exhibit such a shoulder but no other noble gases have been investigated. In this section we briefly analyze the existence of the shoulder in the Coulomb hole of other noble gases and isoelectronic ions using a basis set that is known to produce the shoulder structure. CISD/6-311G$^*$ Coulomb hole plots of 10-, 18-, and 36-electron systems are displayed in Fig. 6. The ten-electron systems exhibit a shoulder in the Coulomb hole for various effective nuclear charges, $Z = 8 - 11$. Ar has an atomic structure with three complete shells: K, L and M. Interestingly, this noble gas and its ions, Cl$^-$ and K$^+$, also show a shoulder or a small minimum at the short-range region of the Coulomb hole. Kr atom and Br$^-$, which complete four shells up to N, display a non-smooth region at short distances that also seems to be caused by the correlation effects of the core 1s electrons. Interestingly, the shoulder is also present in the short-range part of the Coulomb hole of noble-gas molecules, such as Ne$_2$ (see Fig. S10).

IV. CONCLUSIONS

We have analyzed the Coulomb hole of Ne from highly-accurate CISD wave functions. Our energy estimates have been obtained from a two-fold extrapolation of optimized even-tempered basis sets and compare well with the best estimates available in the literature (we recover 97% of the correlation energy of Ne).

We have confirmed the existence of a shoulder in the short-range region of the Coulomb hole of the Ne atom, which is due to the correlation of the core electrons in the K shell. Double excitations from the core orbital give rise to the most important configurations in the CISD expansion that contribute to the shoulder. The shoulder is due to an internal reorganization of the K shell, where electrons are pushed towards the K-shell boundary. The correlation nature of the shoulder is dynamic, as one would expect.

The feature is not displayed in the Coulomb hole cal-
culated with certain basis sets, such as the correlated-consistent basis set of Dunning, shedding some doubts on the quality of the description of the core electrons using these basis sets.

FIG. 6. The CISD/6-311G* Coulomb holes of Ne, Ar and Kr, as well as some isoelectronic ions.

The short-range shoulder of the Coulomb hole seems to be a phenomenon that goes beyond the Ne atom and extends to larger noble gases, their ions and noble-gas molecules. This feature apparently shows in species that benefit from the extra stabilization provided by a closed-shell structure with no valence electrons, and it is not modified by increase or decrease of the strength of the Coulombic nuclear-electron potential. Further investigation in this line is currently being conducted in our laboratories.

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