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Calculation of Araki-Sucher correction for many-electron systems

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We consider the evaluation of the Araki-Sucher correction for arbitrary many-electron atomic and molecular systems. This contribution appears in the leading-order quantum electrodynamics corrections to the energy of a bound state. The conventional one-electron basis set of Gaussian-type orbitals is adopted; this leads to two-electron matrix elements which are evaluated with the help of the generalized McMurchie-Davidson scheme. We also consider the convergence of the results towards the complete basis set. A rigorous analytic result for the convergence rate is obtained and verified by comparing with independent numerical values for the helium atom. Finally, we present a selection of numerical examples and compare our results with the available reference data for small systems. In contrast with other methods used for the evaluation of the Araki-Sucher correction, our method is not restricted to few-electron atoms or molecules. This is illustrated by calculations for several many-electron atoms and molecules.

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I. INTRODUCTION

In the past few decades, there has been remarkable progress in the many-body electronic structure theory. This has allowed researchers to treat large systems of chemical or biological significance containing hundreds of electrons and, at the same time, obtain very accurate results for small systems which are intensively studied spectroscopically. The introduction of general explicitly correlated methods [1–3], reliable extrapolation techniques [4–9], general coupled-cluster theories [10,11], and new or improved one-electron basis sets [12–22] has made the so-called spectroscopic accuracy (few cm^{-1} or less) achievable for many small molecules.

However, as the accuracy standards of routine calculations are tightened up, one encounters new challenges. One of these challenges is the necessity to include corrections due to the finite mass of the nuclei [23], relativistic, and quantum electrodynamic (QED) effects [24], and possibly finite nuclear size [25]. The former two have been the subjects of many studies in past decades; see Refs. [26–33] and references therein. However, systematic studies of importance of the QED effects in atoms and molecules are scarce and have begun relatively recently [34–36]. High accuracy of the *ab initio* calculations and reliability of the theoretical predictions is of prime importance, e.g., in the field of ultracold molecules. This is best illustrated by the papers of McGuyer *et al.* [37], which are devoted to observation of the subradiant states of Sr_2, or by McDonald and collaborators [38], where photodissociation of ultracold molecules was studied. Notably, the importance of QED effects has also been realized in the first-principles studies of He_2 for the purposes of metrology [39–41].

QED is definitely one of the most successful theories in physics, with calculation of the anomalous magnetic moment of the electron being the prime example [42–44]. However, applications to the bound states, e.g., with a strong Coulomb field, are marred with problems. Two physical phenomena, i.e., electron self-energy and vacuum polarization, giving rise to the Lamb shift [24] are difficult to include in the standard many-body theories. For moderate and large-Z approaches based on the Uehling potential [45] with optional corrections [46,47], scaling of the hydrogenlike values [48,49], effective potentials of Shabaev *et al.* [50,51], multiple commutator approach by Labzowsky and Goidenko [52,53], and effective Hamiltonians of Flambaum and Ginges [54] were used with considerable success.

However, for small and moderate Z, the most theoretically consistent approach is the nonrelativistic QED theory (NRQED) proposed by Caswell and Lepage [55] and further developed and extended by Pachucki [56–59]. This method relies on the expansion of the exact energy in power series of the fine-structure constant, α. The coefficients of the expansion are evaluated as expectation values of an effective Hamiltonian with the nonrelativistic wave function. Thus, the zeroth-order term is simply the nonrelativistic energy, the first-order term is zero, and the second-order contributions are expectation values of the Breit-Pauli Hamiltonian (the relativistic corrections).

NRQED has been successfully applied to numerous few-electron atomic and molecular systems. Obvious applications are the one-electron systems such as hydrogenlike atoms (see Ref. [60] for a comprehensive review) and the hydrogen molecular ion [61–65]. Beyond that, very accurate results are available for the helium atom [66–77], hydrogen molecule [78–83], and their isotopomers. Remarkably, corrections of the order of α^4 have been derived and evaluated recently [72,83–85]. Other examples are lithium [86–88] and beryllium atoms [89] with the corresponding ions [85], and helium dimer [39,40,90]. In all of these examples, very accurate agreement with the experimental data has been obtained, which confirms the validity and applicability of NRQED to light molecular and atomic systems. However, all presently available rigorous methods for calculation of the NRQED corrections are inherently limited to few-body systems and cannot be straightforwardly extended to larger ones.

In the framework of NRQED, the leading (pure) QED corrections are of the order of α^3 and $\alpha^3 \ln \alpha$. For a singlet

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atomic or molecular state, one has [91,92]

$$E^{(3)} = \frac{8\alpha}{3\pi}\left(\frac{19}{30} - 2\ln\alpha - \ln k_0\right)\langle D_1\rangle + \frac{\alpha}{\pi}\left(\frac{164}{15} + \frac{14}{3}\ln\alpha\right)\langle D_2\rangle + \langle H_{AS}\rangle, \quad (1)$$

where $\ln k_0$ is the so-called Bethe logarithm [24,66]; $\langle D_1\rangle$ and $\langle D_2\rangle$ are the one- and two-electron Darwin terms,

$$\langle D_1\rangle = \frac{\pi}{2}\,\alpha^2 \sum_a Z_a\left\langle \sum_i \delta(\mathbf{r}_{ia})\right\rangle, \quad (2)$$

$$\langle D_2\rangle = \pi\,\alpha^2\left\langle \sum_{i>j} \delta(\mathbf{r}_{ij})\right\rangle, \quad (3)$$

where Z_a are the nuclear charges, and $\delta(\mathbf{r})$ is the three-dimensional Dirac delta distribution. Throughout the paper, we use letters $i,j,\dots$ and $a,b,\dots$ to denote summations over electrons and nuclei, respectively. The last term in Eq. (1) is the Araki-Sucher (AS) correction,

$$\langle H_{AS}\rangle = -\frac{7\alpha^3}{6\pi}\left\langle \sum_{i>j} \hat{P}\left(r_{ij}^{-3}\right)\right\rangle, \quad (4)$$

where the regularized distribution in the brackets is defined by the following formulas:

$$\hat{P}\left(r_{ij}^{-3}\right) = \lim_{a\to 0} \hat{P}_a\left(r_{ij}^{-3}\right) \quad (5)$$

and

$$\hat{P}_a\left(r_{ij}^{-3}\right) = \theta(r_{ij} - a)\, r_{ij}^{-3} + 4\pi(\gamma + \ln a)\delta(\mathbf{r}_{ij}), \quad (6)$$

where γ is the Euler-Mascheroni constant, and $\theta(x)$ is the Heaviside step function in the usual convention.

In evaluation of the QED corrections for many-electron atoms and molecules, two quantities present in Eq. (1) are the major source of difficulties. The first one is the Bethe logarithm and the second is the Araki-Sucher correction. In this paper, we are concerned with the latter quantity; evaluation of the Bethe logarithm will be considered in subsequent papers. Let us point out that the Araki-Sucher term is not necessarily the largest of the α^3 QED corrections. In fact, the one-electron terms typically dominate in Eq. (1). However, the relative importance of the Araki-Sucher correction is expected to increase for heavier atoms similarly as for the two-electron terms of the Breit-Pauli Hamiltonian. Moreover, for polyatomic systems, the Araki-Sucher correction possesses an usual R^{-3} asymptotics for large interatomic distances R. As a result, it decays much less rapidly than the other components of the potential energy curve [93] and its importance is substantial for large R.

From the point of view of the many-body electronic structure theory, Eq. (4) is an ordinary expectation value of a two-electron operator. Provided that the corresponding matrix elements are available, evaluation of such expectation values by using the coupled-cluster (CC) [94] or configuration-interaction (CI) wave functions is a standard task [95–102]. Therefore, in this work, we are concerned with evaluation of the matrix elements (i.e., two-electron integrals) of the Araki-Sucher distribution in the Gaussian-type orbitals (GTOs) basis [103]. Importantly, the proposed method can be applied to an arbitrary molecule and is not limited to few-electron systems.

Throughout the paper, we follow Ref. [104] in definitions of all special and elementary functions.

II. CALCULATION OF THE MATRIX ELEMENTS

In this section, we consider evaluation of the matrix elements that are necessary to calculate the Araki-Sucher correction for many-electron atomic and molecular systems. We adopt the usual Gaussian-type orbitals (GTOs) in the Cartesian representation [103] as the one-electron basis set,

$$\phi_a(\mathbf{r}_A) = x_A^i\, y_A^k\, z_A^m\, e^{-ar_A^2}, \quad (7)$$

where $\mathbf{A} = (A_x, A_y, A_z)$ is a vector specifying the location of the orbital, $x_A = x - A_x$, and similarly for the remaining coordinates. For brevity, we omit the normalization constant in definition (7). However, normalized orbitals are used in all calculations described further in the paper.

Evaluation of the Araki-Sucher correction from the many-electron coupled-cluster wave function within the basis set (7) requires the following two-electron matrix elements:

$$(ab|cd) = \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_a(\mathbf{r}_{1A})\,\phi_b(\mathbf{r}_{1B})\hat{P}\left(r_{12}^{-3}\right)\phi_c(\mathbf{r}_{2C})\,\phi_d(\mathbf{r}_{2D}). \quad (8)$$

The scheme presented further in the paper relies on the McMurchie-Davidson method [105,106]. This method was first introduced in the context of the standard two-electron repulsion integrals and various one-electron integrals necessary for calculation of the molecular properties. Later, it was extended to handle integral derivatives and more-involved two-electron integrals found in the so-called explicitly correlated methods [107,108]. While some other methods of calculation of the usual electron repulsion integrals are more computationally efficient (cf. Ref. [109]) than the McMurchie-Davidson scheme, the latter is much simpler to implement and extend to more complicated integrals. This was the main motivation for its use in the present context.

A. Generalized McMurchie-Davidson scheme

The backbone of the McMurchie-Davidson scheme is the so-called Gauss-Hermite function $\Lambda_t(x;a)$ defined formally as

$$\Lambda_t(x_A;a)\exp\left(-ax_A^2\right) = \partial_{A_x}^t \exp\left(-ax_A^2\right). \quad (9)$$

Clearly, the functions $\Lambda_t(x;a)$ are closely related (by scaling) with the well-known Hermite polynomials. It is also straightforward to prove the following relation:

$$x_A^i x_B^j\, e^{-ax_A^2}\, e^{-bx_B^2} = e^{-px_P^2} \sum_{t=0}^{i+j} E_t^{ij}\,\Lambda_t(x_P;p), \quad (10)$$

where $p = a + b$ and $\mathbf{P} = \frac{a\mathbf{A}+b\mathbf{B}}{p}$. The coefficients E_t^{ij} can be calculated with convenient recursion relations [105,106].

With the help of Eqs. (9) and (10), one can show that the product of two off-centered GTOs can be written as

$$\phi_a(\mathbf{r}_A)\phi_b(\mathbf{r}_B) = \sum_{t=0}^{i+j} E_t^{ij} \sum_{u=0}^{k+l} E_u^{kl} \sum_{v=0}^{m+n} E_u^{mn} \times \partial_{P_x}^t \, \partial_{P_y}^u \, \partial_{P_z}^v \, \exp\left(-pr_P^2\right). \tag{11}$$

We return to the initial integrals (8) and use Eq. (11) for both orbital products. This leads to

$$(ab|cd) = \sum_{t=0}^{i+j} E_t^{ij} \sum_{u=0}^{k+l} E_u^{kl} \sum_{v=0}^{m+n} E_u^{mn} (-1)^{t+u+v} \times \sum_{t'=0}^{i'+j'} E_{t'}^{i'j'} \sum_{u'=0}^{k'+l'} E_{u'}^{k'l'} \sum_{v'=0}^{m'+n'} E_{u'}^{m'n'} \times R^{t+t',u+u',v+v'}, \tag{12}$$

where

$$R^{tuv} = \partial_{Q_x}^t \, \partial_{Q_y}^u \, \partial_{Q_z}^v \, B, \tag{13}$$

and B is the so-called *basic integral* defined as $B = \lim_{a\to 0} B_a$ with

$$B_a = \iint d\mathbf{r}_1 \, d\mathbf{r}_2 \, \exp\left(-pr_{1P}^2\right) \hat{P}_a\left(r_{12}^{-3}\right) \exp\left(-qr_{2Q}^2\right). \tag{14}$$

Note that differentiation with respect to the coordinates of $\mathbf{P}$ in Eq. (12) has been replaced by differentiation with respect to the corresponding components of $\mathbf{Q}$. This is valid because the basic integral is dependent only on the length of $\mathbf{P}-\mathbf{Q}$ but not on the individual components.

The biggest inconvenience connected with Eq. (13) is the necessity to differentiate with respect to Cartesian coordinates. In the original treatment of McMurchie and Davidson (concerning the standard electron repulsion integrals), a four-dimensional recursion relation was introduced to resolve this issue [105,106]. This approach is difficult to generalize to other basic integrals and typically requires a separate treatment in each case. In a recent paper, we proposed a different strategy based on the following expression [108]:

$$x^t y^u z^v = \sum_{l=0}^{l_{\max}} \sum_{m=-l}^{l} c_{tuv}^{lm} \, r^{l_{\max}-l} Z_{lm}(\mathbf{r}), \tag{15}$$

where $l_{\max} = t+u+v$, relating Cartesian coordinates with the real solid spherical harmonics, $Z_{lm}(\mathbf{r}) = r^l \, Y_{lm}(\hat{r})$ (note that the Racah normalization is not adopted here). The numerical coefficients c_{tuv}^{lm} can be precalculated and stored in memory as a look-up table (cf. the work of Schlegel [110]). In analogy, the differentials present in Eq. (13) are rewritten as

$$\partial_{Q_x}^t \, \partial_{Q_y}^u \, \partial_{Q_z}^v = \sum_{l=0}^{l_{\max}} \sum_{m=-l}^{l} c_{tuv}^{lm} \, \nabla_Q^{l_{\max}-l} \, \hat{Z}_{lm}(\nabla_Q), \tag{16}$$

where ∇_Q is the gradient operator and $\hat{Z}_{lm}(\nabla_Q)$ are the (real) spherical harmonic gradient operators [111]. Heuristically, they are obtained by taking an explicit expression for $Z_{lm}(\mathbf{r})$ and replacing all Cartesian coordinates with the corresponding differentials.

By virtue of the Hobson theorem [112], one has

$$\hat{Z}_{lm}(\nabla_Q)g(Q) = \left[D_Q^l \, g(Q)\right] Z_{lm}(\mathbf{Q}), \tag{17}$$

where $D_Q = Q^{-1}\partial_Q$, for an arbitrary function $g(Q)$ dependent only on the length of the vector, Q. With the help of Eqs. (16) and (17), one can write

$$R^{tuv} = \sum_{l=0}^{l_{\max}} \sum_{m=-l}^{l} c_{tuv}^{lm} \, \nabla_Q^{l_{\max}-l} \left[\left(D_Q^l \, B\right) Z_{lm}(\mathbf{Q})\right]. \tag{18}$$

Note that the quantity in the subscript, $l_{\max}-l$, is always even (otherwise the coefficients c_{tuv}^{lm} vanish). Therefore, the last step amounts to repeated action of the Laplacian on the terms in the square brackets. The final result can be obtained by noting that the solid harmonics are eigenfunctions of the Laplace operator and by using the obvious relationship $\nabla_Q^2 = Q^2 D_Q^2 + 3D_Q$ for the radial part of the integrations,

$$R^{tuv} = \sum_{l=0}^{l_{\max}} \sum_{m=-l}^{l} c_{tuv}^{lm} \, Z_{lm}(\mathbf{Q}) \sum_{k=0}^{k_{\max}} d_k^{l,k_{\max}} \times \left(D_Q^{l_{\max}-k} \, B\right) Q^{l_{\max}-l-2k}, \tag{19}$$

where $k_{\max} = \frac{1}{2}(l_{\max}-l)$. The auxiliary coefficients d_n^{lm} are calculated recursively,

$$d_n^{lm} = d_n^{l,m-1} + [2l+3+4(m-n)]d_{n-1}^{l,m-1} + 2(m-n+1)[2l+3+2(m-n)]d_{n-2}^{l,m-1}, \tag{20}$$

starting with $d_0^{lm} = 1$; the last term of the recursion is neglected for $n = 1$. Note that the coefficients d_n^{lm} can also be stored as a look-up table.

To sum up, by means of Eq. (19) all integrals R^{tuv} are expressed through the derivatives of the basic integral, $D_Q^l B$. We consider evaluation of these quantities in the next section. Let us also note in passing that to achieve an optimal efficiency during the evaluation of Eq. (19), the summations need to be carried out stepwise, paying attention to the order of the individual sums.

B. Basic integral and derivatives

Calculation of the basic integral, given formally by the limit of Eq. (14), is hampered by the troublesome form of the Araki-Sucher distribution. It was shown in Ref. [108] that an equivalent general formula for the basic integral reads

$$B_a = e^{-qQ^2} \iint d\mathbf{r}_1 d\mathbf{r}_2 \, e^{-qr_2^2 - pr_1^2} \, i_0(2qQr_2) \, \hat{P}_a\left(r_{12}^{-3}\right), \tag{21}$$

where $i_0(x) = \sinh x/x$. In the present case, this expression naturally splits into two parts, $B_a = B_a^{(1)} + B_a^{(2)}$,

$$B_a^{(1)} = e^{-qQ^2} \iint d\mathbf{r}_1 d\mathbf{r}_2 \, \frac{\theta(r_{12}-a)}{r_{12}^3} e^{-qr_2^2 - pr_1^2} \, i_0(2qQr_2), \tag{22}$$

$$B_a^{(2)} = 4\pi \, e^{-qQ^2}(\gamma + \ln a) \int d\mathbf{r} \, e^{-(p+q)r^2} \, i_0(2qQr), \tag{23}$$

where the second formula follows directly from the properties of the Dirac delta distribution. The first integral can be simplified by changing the coordinates to r_1, r_2, r_{12} and three arbitrary angles. Integration over all variables apart from r_{12} is elementary,

$$B_a^{(1)} = \sqrt{\frac{\pi^5}{p+q}}\frac{1}{pq}\int_a^\infty \frac{dr}{r^2}\,\frac{e^{-\xi(r-Q)^2} - e^{-\xi(r+Q)^2}}{Q}, \quad (24)$$

where $\xi = \frac{pq}{p+q}$. The next step is to expand the Q-dependent part of the integrand into a power series,

$$B_a^{(1)} = 2\mathcal{N} e^{-\xi Q^2}\sum_{n=0}^{\infty}\frac{(2\xi Q)^{2n}}{(2n+1)!}\int_a^\infty dr r^{2n-1}e^{-\xi r^2}, \quad (25)$$

where $\mathcal{N} = 2\pi\,(\frac{\pi}{p+q})^{3/2}$. The first term of the series (corresponding to $n = 0$) must be extracted and treated separately, but the remaining integrals are straightforward. Importantly, to simplify the integration process, we drop all higher-order terms in a which do not contribute to the final result (once the $a \to 0$ limit is taken). After integration and some rearrangements, one obtains

$$B_a^{(1)} = 2\mathcal{N}\, e^{-\xi Q^2}\bigg[-\frac{\gamma}{2} - \ln a - \frac{\ln\xi}{2} + \frac{1}{2}\sum_{n=1}^{\infty}\frac{4^n(n-1)!}{(2n+1)!}(\xi Q^2)^n\bigg] + O(a). \quad (26)$$

Let us return to the second part of the basic integral $B_a^{(2)}$. Fortunately, this integration is elementary,

$$B_a^{(2)} = 2\mathcal{N} e^{-\xi Q^2}(\gamma + \ln a). \quad (27)$$

Let us now add both contributions and take the limit $a \to 0$. The logarithmic singularities present in $B_a^{(1)}$ and $B_a^{(2)}$ cancel out, and the result reads

$$B = \mathcal{N} e^{-\xi Q^2}\bigg[\gamma - \ln\xi + \sum_{n=1}^{\infty}\frac{4^n(n-1)!}{(2n+1)!}(\xi Q^2)^n\bigg]. \quad (28)$$

One can easily prove that the infinite series present in the above expression is convergent for an arbitrary real ξQ^2. Therefore, this formula constitutes an exact analytical result. However, the rate of convergence of this series can be expected to be very slow for large values of the parameter, greatly increasing the cost of the calculations. Moreover, this representation does not allow for a straightforward calculation of the derivatives, D^l_Q. Therefore, it is desirable to bring this expression into a more computationally convenient form.

For this sake, the series in Eq. (28) is summed analytically, giving the following integral representation:

$$\sum_{n=1}^{\infty}\frac{4^n(n-1)!}{(2n+1)!}x^n = \int_0^1 dt\,(1-t)^{1/2}\,\frac{e^{tx}-1}{t}. \quad (29)$$

Validity of this formula can easily be verified by expanding the integrand into a power series in x and integrating term by term. Guided by Eq. (29), one can introduce a more general family of functions,

$$J_l(x) = e^{-x}\int_0^1 \frac{dt}{t}(1-t)^{1/2}[e^{tx}(1-t)^l - 1]. \quad (30)$$

Note that $J_0(x)$ directly corresponds to the result of the summation in Eq. (29) and $J_l(x) = -\partial_x J_{l-1}(x)$. With the help of the newly introduced quantities, the basic integral is rewritten as

$$B = \mathcal{N}[e^{-\xi Q^2}(\gamma - \ln\xi) + J_0(\xi Q^2)]. \quad (31)$$

Within this particular representation of the basic integral, it becomes disarmingly simple to perform the required differentiation. In fact, one can show that

$$D^l_Q B = \mathcal{N}(-2\xi)^l[e^{-\xi Q^2}(\gamma - \ln\xi) + J_l(\xi Q^2)], \quad (32)$$

which completes the present section. Parenthetically, we note that in the above formula, the argument of J_l is always positive, i.e., $\xi Q^2 > 0$, despite the fact that the formal definition of these integrals given by Eq. (30) is valid for an arbitrary complex-valued x.

At this point, we would like to compare our results with some other expressions published in the literature. An integral closely related to the basic integral B was considered in Ref. [81]. In fact, one can verify that by setting $c_1 = c_2 = 0$ in Eq. (15) of Ref. [81], one obtains Eq. (14) of the present work (after taking the $a \to 0$ limit). However, no results for the derivatives $D^l_Q B$ were provided as they do not appear in the explicitly correlated Gaussian calculations. Interestingly, an alternative integral representation of $J_0(x)$ was given in Ref. [81]. In our notation,

$$J_0(x) = e^{-x}\int_0^x \frac{dt}{t}\bigg[\sqrt{\frac{\pi}{t}}\frac{e^t}{2}\,\mathrm{erf}(\sqrt{t}) - 1\bigg], \quad (33)$$

where erf(x) is the error function. One can verify that the definitions (30) and (33) coincide by exchanging the variables and working out the inner integral. We have not found the above representation particularly useful in the present context, but it provides an additional verification that our final result is correct.

C. Auxiliary integrals $J_l(x)$

The only missing building block of the present theory is the calculation of the integrals $J_l(x)$. First, let us specify the range of parameters (x and l) which are of interest. The maximal value of l is set to 32 in our program. This allows one to compute the integrals (8) with the maximal value $i + k + m = 8$ in the one-electron basis set; see Eq. (7). This corresponds to the maximal value of the angular momentum $l = 8$ (L-type functions) in a purely spherical representation. The are no limitations on the value of $x \geqslant 0$, i.e., the code is open ended with respect to positive values of x. Below, we provide a set of procedures based mostly on the recursive relations which allow one to calculate the integrals $J_l(x)$ with accuracy of at least 12 significant digits over the whole range of parameters specified above.

First, for $x = 0$, the integrals $J_l(x)$ take a particularly simple analytic form,

$$J_l(0) = 2 - 2\ln 2 - H_{l+1/2}, \quad (34)$$

where H_n are the harmonic numbers. This expression can be rewritten as a convenient recursion, $J_{l+1}(0) = J_l(0) - \frac{2}{2l+3}$, starting with $J_0(0) = 0$. The values of $J_l(0)$ constitute an important special case corresponding to the atomic integrals, but they appear in large numbers also in molecular calculations.

For any value of x, the integrals $J_l(x)$ obey the following recursion relation:

$$J_{l+1}(x) = J_l(x) - 2F_{l+1}(x), \tag{35}$$

where

$$F_n(T) = \int_0^1 dt t^{2n} e^{-Tt^2}. \tag{36}$$

The latter quantity is simply the famous Boys function [103] that has been considered a countless number of times in the quantum chemistry literature (see, for example, Refs. [113–116] and references therein). Accurate and efficient methods for calculation of $F_n(T)$ are available and there is no reason for us to elaborate on this issue.

Returning to the recursion relation (35), its direct use is hampered by a peculiar behavior of the integrals $J_l(x)$. Let us temporarily consider l to be a continuous variable. Then, for any fixed $x > 0$, the integrals $J_l(x)$ have a root as a function of l. For brevity, let us call the exact position of the root (as a function of x) the *critical line*, $l_0(x)$. The exact location of the root cannot be obtained with elementary methods, but we found that a simple linear function,

$$l_0(x) = 0.44 + 1.17x, \tag{37}$$

provides a reasonably faithful picture. If the recursion (35) is carried out and the critical line is crossed, one can expect an unacceptable loss of significant digits due to the cancellations. Therefore, this simple approach is inherently numerically unstable, independently of whether the recursion is carried out upward or downward.

One of the possible solutions to this problem is to assert that the critical line is never crossed during the recursive process. This can be achieved as follows. For an interval of x of approximately unit length, we find the smallest value of l *above* the critical line (l_a) and the largest value of l *below* the critical line (l_b). Starting from the value at l_a, the upward recursion is initiated and carried out up to the maximal desired value of l. Similarly, the downward recursion is initiated at l_b and stopped at $l = 0$. This guarantees that the integrals $J_l(x)$ do not change sign in both subrecursions and the whole process is completely numerically stable since the integrals $F_l(x)$ are always positive.

The remaining problem is to evaluate the integrals $J_l(x)$ at l_a and l_b for a given x. This is achieved by fitting $J_{l_a}(x)$ and $J_{l_b}(x)$ for each interval of x. Since the length of each interval is only about unity, the ordinary exponential-polynomial [117] fitting is sufficient, i.e.,

$$e^{-x} \sum_{k=0}^{N_{\rm fit}} c_k^{(1)} x^k. \tag{38}$$

The length of the expansion was chosen to be $N_{\rm fit} = 11$ in each interval, both for l_a and l_b.

For $x > x_0 \approx 36$, the method described above needs to be slightly modified. This is the point where the critical line crosses $l = 32$. Therefore, for $x > x_0$, all $J_l(x)$ with $l \leqslant 32$ are positive, and it is sufficient to evaluate $J_{32}(x)$ by fitting and carry out the recursion (35) downward. We used the following fitting function:

$$\sum_{k=0}^{N'_{\rm fit}} c_k^{(2)} x^k + \frac{1}{x^{81/2}} \sum_{k=0}^{N'_{\rm fit}} c_k^{(3)} x^k, \tag{39}$$

with $N'_{\rm fit} = 9$. The prefactor in the second term of this expression comes from the asymptotic expansion of J_l, which will be introduced in the next paragraph.

Finally, for $x > x_{\rm asym}$, we use large-x asymptotic expansion of the $J_l(x)$ functions. For $l = 0$, the necessary expression was given in Ref. [81],

$$J_0(x) = \frac{\sqrt{\pi}}{2x^{3/2}} \sum_{k=0} \frac{(2k+1)!!}{2^k} x^{-k}, \tag{40}$$

and, for larger l, the corresponding formulas can be obtained by noting that $J_l(x) = -\partial_x J_{l-1}(x)$. The value of $x_{\rm asym}$ was set to 125 after some numerical experimentation. Under these conditions, the summation converges to the machine precision after at most 30 terms. In general, the rate of convergence improves with increasing x and thus expansion (40) is able to handle arbitrarily large values of $x > x_{\rm asym}$. Moreover, all terms in Eq. (40) are positive and thus no loss of digits in the summation is possible. This observation remains valid for $l > 0$.

To sum up, the integrals $J_l(x)$ are calculated with a union of three algorithms, involving polynomial fitting, recursion relations, and asymptotic expansion. We note that the efficiency of the resulting code is only somewhat worse than for the aforementioned Boys function. A C++ implementation of the methods described in this section can be obtained upon request.

III. BASIS-SET CONVERGENCE ISSUE

Most of the *ab initio* methods used nowadays in the electronic structure theory rely on a basis set for expansion of the exact wave function. Consequently, observables obtained with a (necessarily finite) basis set suffer from the basis-set incompleteness error. To allow for a meaningful comparison with the experimental data, this error should be estimated and minimized, if possible.

One of the prominent techniques applied to remove a bulk fraction of the basis-set incompleteness error is the extrapolation towards the exact theoretical value. However, to ensure that such a procedure is reliable, one typically requires some information on how the calculated values converge towards the exact result as a function of the basis-set size. For example, it was shown by Hill [118] that the nonrelativistic energy converges as L^{-3}, where L is the largest angular momentum present in the basis set. It can be shown that some relativistic corrections converge even slower, as L^{-1}. This was numerically observed in Refs. [119,120] and later proved by Kutzelnigg [121]. In this case, the values calculated with a finite basis set can be in error of tens of percents and extrapolation is necessary to arrive at a reliable result.

Concerning the Araki-Sucher correction, here we assess how the results obtained with finite basis sets converge as a function of the largest angular momentum included. To answer this question, we consider the ground state of the helium atom as a model system where a strict asymptotic result can be obtained. Further in the paper, we show numerically that the main conclusions are valid also for many-electron, many-center systems. This allows for a reliable extrapolation towards the complete basis-set limit, dramatically improving the final results.

A. Definitions and notation

We consider the ground 1^1S state of the helium atom with the exact wave function given by $\Psi(\mathbf{r}_1,\mathbf{r}_2)$, where $\mathbf{r}_i$ are the positions of the electrons and $\mathbf{r}_{12}=\mathbf{r}_1-\mathbf{r}_2$. The corresponding wave function can be represented as

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\sum_{l=0}^{\infty}\Psi_l(r_1,r_2)P_l(\cos\theta_{12}),\qquad(41)$$

where $r_i=|\mathbf{r}_i|$, P_l are the Legendre polynomials, and θ_{12} is the angle between vectors $\mathbf{r}_1$ and $\mathbf{r}_2$. The above expression is dubbed *the partial wave expansion* (PWE) by many authors and we shall follow this nomenclature for the wave functions and operators.

It is natural to define a family of approximants to the exact wave function by truncating Eq. (41) at a given L, i.e.,

$$\Psi_L(\mathbf{r}_1,\mathbf{r}_2)=\sum_{l=0}^{L}\Psi_l(r_1,r_2)P_l(\cos\theta_{12}).\qquad(42)$$

The Araki-Sucher correction can then be approximated as the $a\to 0$ limit of the following expectation values:

$$\big\langle\hat{P}_a\big(r_{ij}^{-3}\big)\big\rangle_L=\big\langle\Psi_L\big|\hat{P}_a\big(r_{ij}^{-3}\big)\big|\Psi_L\big\rangle/\langle\Psi_L|\Psi_L\rangle.\qquad(43)$$

Obviously, in the infinite-L limit, this series converges to the exact value, $\langle\hat{P}_a(r_{ij}^{-3})\rangle$. Therefore, we may consider the error

$$\epsilon_L(a)=\big\langle\hat{P}_a\big(r_{ij}^{-3}\big)\big\rangle-\big\langle\hat{P}_a\big(r_{ij}^{-3}\big)\big\rangle_L\qquad(44)$$

as a function of L and ask what is the asymptotic form of $\epsilon_L(a)$ at large L. After taking the $a\to 0$ limit, one recovers the actual result for the Araki-Sucher correction. This is only a precise mathematical restatement of the intuitive picture presented at the beginning of this section.

All derivations presented further rely on the seminal work of Hill and the methods introduced therein [118]. The original presentation of Hill relies on a chain of postulates which is extremely difficult to prove strictly, but is nonetheless very physically sound and hard to deny (especially in the face of ample numerical evidence). First, the denominator in Eq. (43) can be replaced by unity as it converges much faster than the numerator and does not contribute in the leading order. Second, for large L, the dominant contribution to the integral in Eq. (43) comes from the region around the electrons' coalescence points. The famous Kato cusp condition [122] teaches us that in this regime, the exact wave function behaves as

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\Psi(r,r,0)\big(1+\tfrac{1}{2}r_{12}\big)+O\big(r_{12}^2\big),\qquad(45)$$

where $\Psi(r,r,0)$ is the value of the exact wave function at $r_{12}=0$. By using these assumptions, modulus square of the present wave function is rewritten as

$$|\Psi(\mathbf{r}_1,\mathbf{r}_2)|^2=|\Psi(r,r,0)|^2(1+r_{12})+O\big(r_{12}^2\big).\qquad(46)$$

Finally, let us recall PWE for r_{12},

$$r_{12}=\sum_{l=0}^{\infty}\{r_{12}\}_l\,P_l(\cos\theta_{12}),\qquad(47)$$

$$\{r_{12}\}_l=\frac{1}{2l+3}\frac{r_<^{l+2}}{r_>^{l+1}}-\frac{1}{2l-1}\frac{r_<^{l}}{r_>^{l-1}},\qquad(48)$$

where $r_<=\min(r_1,r_2)$, $r_>=\max(r_1,r_2)$. This expression is closely related to the well-known Laplace expansion of the potential.

B. PWE for the Araki-Sucher distribution

Throughout the presentation, we shall need PWE for the distribution of Eq. (6),

$$\widehat{P}_a\big(r_{12}^{-3}\big)=\sum_{l=0}^{\infty}\mathcal{A}_l(r_1,r_2;a)\,P_l(\cos\theta_{12}),\qquad(49)$$

where the radial coefficients are defined formally through the expression

$$\mathcal{A}_n(r_1,r_2;a)=\frac{2n+1}{2}\int_0^{\pi}d\theta_{12}\,\sin\theta_{12}\,\widehat{P}_a\big(r_{12}^{-3}\big)P_n(\cos\theta_{12}).\qquad(50)$$

Derivation of the explicit expression for $\mathcal{A}_l(r_1,r_2;a)$ is fairly straightforward and relies solely on Eq. (50). However, it requires some tedious technical algebra. In order to shorten the main text, we present the entire derivation in the Appendix A. Herein, we present only the final result,

$$\mathcal{A}_n(r_1,r_2;a)=\mathcal{A}_n'(r_1,r_2;a)+\mathcal{A}_n''(r_1,r_2;a)+\mathcal{A}_n'''(r_1,r_2;a)+O(a),\qquad(51)$$

where

$$\mathcal{A}_n'(r_1,r_2;a)=\theta(|r_1-r_2|-a)\frac{(2n+1)r_<^n r_>^{-n-1}}{r_>^2-r_<^2},\qquad(52)$$

$$\mathcal{A}_n''(r_1,r_2;a)=\theta(a-|r_1-r_2|)\theta(r_1+r_2-a)\times\frac{2n+1}{2a}\frac{1}{r_1r_2}P_n\bigg(\frac{r_1^2+r_2^2}{2r_1r_2}\bigg),\qquad(53)$$

and

$$\mathcal{A}_n'''(r_1,r_2;a)=(2n+1)(\gamma+\ln a)r_1^{-2}\,\delta(r_1-r_2).\qquad(54)$$

Note that only the leading-order terms in a have been retained in the above formulas. This is justified because the actual Araki-Sucher correction of Eq. (5) involves the $a\to 0$ limit and all higher-order contributions in a vanish.

C. Large-L asymptotic formula for $\epsilon_L(a)$

Let us insert Eqs. (46), (47), and (49) into Eq. (43) and change the variables to r_1, r_2, and θ_{12}. Integration over the remaining three variables gives $8\pi^2$ and integration over θ_{12} is trivial due to the orthogonality of the Legendre polynomials. The error is given by

$$\epsilon_L(a)=16\pi^2\sum_{l=L+1}^{\infty}\frac{1}{2l+1}\int_0^{\infty}dr_1\int_0^{\infty}dr_2\times r_1^2r_2^2\,|\Psi(r,r,0)|^2\,\{r_{12}\}_l\,\mathcal{A}_l(r_1,r_2;a),\qquad(55)$$

where the factor $r_1^2\, r_2^2$ comes from the volume element. Let us define the following quantities:

$$I_n'(a) = \frac{1}{2n+1}\int_0^\infty dr_1 \int_0^\infty dr_2\, r_1^2\, r_2^2 \times |\Psi(r,r,0)|^2\, \{r_{12}\}_n\, \mathcal{A}_n'(r_1,r_2;a), \tag{56}$$

which are natural constituents of Eq. (55). Analogous definitions hold for the doubly primed and triply primed quantities in accordance with Eqs. (51)–(54) and for the sum of the three (without the prime).

Starting with Eq. (56), we change the variables to $r_>$ and $r_<$, insert the explicit form of Eqs. (47) and (52), and execute the Heaviside θ to arrive at the result

$$I_n'(a) = 2\int_0^\infty dr_> |\Psi(r_>,r_>,0)|^2 \int_0^{r_>-a} dr_< \times \frac{1}{r_>^2 - r_<^2}\left[\frac{r_<^{2n+4}\, r_>^{-2n}}{2n+3} - \frac{r_<^{2n+2}\, r_>^{2n-2}}{2n-1}\right]. \tag{57}$$

The inner integral can be brought into a closed form, but it is much simpler to obtain the leading-order expression in a from the integration by parts. This leads to

$$I_n'(a) = \frac{4}{(2n-1)(2n+3)}\int_0^\infty dr_>\, r_>^3 \times |\Psi(r_>,r_>,0)|^2\left[\gamma - \frac{1}{2} + \ln\frac{(2n+3)a}{r_>}\right] + O(a), \tag{58}$$

where additionally some higher-order terms in $1/n$ have been neglected.

Passing to the doubly primed quantities, we insert Eq. (53) into Eq. (56) and, after elementary rearrangements and a change of variable, we obtain

$$I_n''(a) = \frac{1}{a}\int_0^\infty dr_> \int_0^{r_>} dr_< |\Psi(r_>,r_>,0)|^2 \times \theta(a - r_> + r_<)\,\theta(r_> + r_< - a) \times P_n\left(\frac{r_>^2 + r_<^2}{2r_>r_<}\right)\left[\frac{r_<^{n+3}\, r_>^{-n}}{2n+3} - \frac{r_<^{n+1}\, r_>^{n-2}}{2n-1}\right]. \tag{59}$$

By the virtues of the θ function, the integral can be rewritten to the form

$$\frac{1}{a}\int_0^\infty dr_> \int_0^{r_>} dr_<\, \theta(a - r_> + r_<)\theta(r_> + r_< - a)\cdots = \frac{1}{a}\left[\int_{a/2}^a dr_> \int_{a-r_>}^{r_>} dr_< + \int_a^\infty dr_> \int_{r_>-a}^{r_>} dr_< \cdots\right]. \tag{60}$$

It turns out that in our case, the first integral gives zero contribution (in the small-a limit). The inner integral of the second component can be expanded as a powers series in a. The first term vanishes and only the second (i.e., proportional to a) has to be retained, giving

$$\int_{r_>-a}^{r_>} dr_<\, P_n\left(\frac{r_>^2 + r_<^2}{2r_>r_<}\right)\left[\frac{r_<^{n+3}\, r_>^{-n}}{2n+3} - \frac{r_<^{n+1}\, r_>^{n-2}}{2n-1}\right] = a\cdot P_n\left(\frac{r_>^2 + r_<^2}{2r_>r_<}\right)\left[\frac{r_<^{n+3}\, r_>^{-n}}{2n+3} - \frac{r_<^{n+1}\, r_>^{n-2}}{2n-1}\right]\Bigg|_{r_<=r_>} = a\cdot\frac{-4\, r_>^3}{(2n-1)(2n+3)} + O(a^2). \tag{61}$$

Upon reinserting into Eq. (59) and rearranging, one obtains

$$I_n''(a) = \frac{-4}{(2n-1)(2n+3)}\int_0^\infty dr_>\, r_>^3 \times |\Psi(r_>,r_>,0)|^2 + O(a). \tag{62}$$

The last integral $I_n'''(a)$ is the simplest to evaluate. One inserts Eq. (54) into Eq. (56) and executes the Dirac δ to arrive at

$$I_n'''(a) = -\frac{4(\gamma + \ln a)}{(2n-1)(2n+3)} \times \int_0^\infty dr_>\, r_>^3\, |\Psi(r_>,r_>,0)|^2, \tag{63}$$

without invoking any approximations. Finally, we add up the three integrals evaluated above,

$$I_n(a) = \frac{1}{4\pi^2}\frac{1}{(2n-1)(2n+3)} \times \left\{\left[\ln(2n+3) - \frac{3}{2}\right]\mathcal{J}_3 - \mathcal{J}_{\ln}\right\} + O(a), \tag{64}$$

where

$$\mathcal{J}_3 = 16\pi^2 \int_0^\infty dr r^3 |\Psi(r,r,0)|^2, \tag{65}$$

$$\mathcal{J}_{\ln} = 16\pi^2 \int_0^\infty dr r^3 \ln r |\Psi(r,r,0)|^2. \tag{66}$$

One can see that in the final expression, all logarithmic singularities cancel out. Therefore, we can now take the limit $a \to 0$, removing all higher-order terms in a.

Let us now return to the formula for the error, given by Eq. (55) at $a = 0$. Making use of Eq. (64) and after some algebra, the result can be written as

$$\epsilon_L(0) = 4\mathcal{J}_3 \sum_{n=L+1}^\infty \frac{\ln(2n+3)}{(2n-1)(2n+3)} - 4\left(\frac{3}{2}\mathcal{J}_3 + \mathcal{J}_{\ln}\right)\sum_{n=L+1}^\infty \frac{1}{(2n-1)(2n+3)}. \tag{67}$$

The first infinite sum is nontrivial to evaluate, but we can utilize the Euler-Maclaurin resummation formula to get the large-L asymptotics. This gives the leading-order expressions and their error estimates,

$$\sum_{n=L+1}^\infty \frac{\ln(2n+3)}{(2n-1)(2n+3)} = \frac{1 + \ln 2L}{4L} + O\left(\frac{\ln L}{L^2}\right), \tag{68}$$

$$\sum_{n=L+1}^\infty \frac{1}{(2n-1)(2n+3)} = \frac{1}{4L} + O(L^{-2}). \tag{69}$$

Finally, we rewrite the error formula as

$$\epsilon_L(0) = \mathcal{J}_3\frac{\ln 2L}{L} - \frac{1}{L}\left(\mathcal{J}_{\ln} + \frac{1}{2}\mathcal{J}_3\right) + O\left(\frac{\ln L}{L^2}\right), \tag{70}$$

which indicates a very slow, i.e., logarithmic, convergence of the Araki-Sucher correction towards the exact value. In fact, the convergence rate is even slower than for the aforementioned relativistic corrections [121]. Nevertheless, the above formula

TABLE I. Total electronic energies and the expectation values of the Araki-Sucher distribution for the helium atom. Extrapolations were performed with the help of Eq. (70) in the case of the Araki-Sucher correction and with the standard X^{-3} formula in the case of the energy [118]. All values are given in atomic units.

Basis	$-E$	$\langle \widehat{P}(r_{12}^{-3}) \rangle$
d3Z	2.90 170	0.470
d4Z	2.90 285	0.541
d5Z	2.90 328	0.595
d6Z	2.90 347	0.637
d7Z	2.90 356	0.670
Extrapolation	2.90 372	1.003
Reference[a]	2.90 372 438	0.989 274

[a]Frolov [128]; all digits shown are correct.

gives precise information on how the values from the finite basis sets should be extrapolated.

IV. NUMERICAL RESULTS

A. Benchmark calculations

To verify that the method of calculation of the matrix elements of the Araki-Sucher distribution and the extrapolation scheme (70) are both valid, we performed calculations for several systems where reference values of this quantity are known to a sufficient accuracy. The includes the helium atom (He), lithium atom (Li) and its cation (Li^+), beryllium atom (Be) and its cation (Be^+), and the hydrogen molecule (H_2). Expectation values of the Araki-Sucher distribution were computed by using the finite-field approach. Suitable values of the displacement parameter were found individually for each system by trial and error. Typically, a value of about 10^{-5} was optimal. For the two- and three-electron systems (He, Li^+, H_2, Li, Be^+), we used the full CI method to solve the electronic Schrödinger equation (this method is exact in the complete basis-set limit). For larger systems, we employed the coupled-cluster single-double and perturbative triple [CCSD(T)] method [123,124]. All electronic structure calculations reported in this work were performed with help of a locally modified version of the GAMESS program package [125,126]. For the helium atom, we used the customized basis sets developed by Cencek *et al.* [90]. For the hydrogen molecule, lithium, and beryllium (both neutral atoms and cations), the standard basis sets developed in Refs. [12,127] were employed.

In Table I, we show results for the calculations for the helium atom. One can see a very slow convergence of the results with the size of the basis set. To overcome this difficulty, we applied a two-point extrapolation formula, given by Eq. (70). Note that in the present case, we do not extrapolate with respect to the maximal angular momentum present in the basis (L), but rather with respect to the so-called cardinal number (X) [12]. This does not change the asymptotic formula (70), but changes values of the numerical coefficients in the expansion. Therefore, we do not attempt to compare the values obtained by fitting with the analytic results given by Eqs. (65) and (66). Nonetheless, the quality of the extrapolation is very good. Extrapolation from the basis sets $X = 3,\ldots,6$ reduces the error from about 30% to less than 1.5% (cf. Table I). One can safely say that the extrapolation is mandatory to obtain results of any reasonable quality.

TABLE II. Expectation values of the Araki-Sucher distribution for the hydrogen molecule (R denotes the internuclear distance). Reference values are given in the third and fourth columns for comparison purposes. All values are given in atomic units.

R	$\langle \widehat{P}(r_{12}^{-3}) \rangle$		
	This work	Ref. [129]	Ref. [81]
0.1	0.8742	0.8707	0.8847
0.6	0.8042	0.7782	0.7775
0.8	0.6857	0.6698	0.6696
1.0	0.6014	0.5714	0.5712
1.4	0.4305	0.4135	0.4143
1.7	0.3356	0.3248	0.3250
2.0	0.2542	0.2550	0.2554
2.6	0.1531	0.1535	0.1555
6.0	0.0060	0.0025	0.0063

Let us now pass to the calculations for the hydrogen molecule H_2. We calculated the Araki-Sucher correction for several internuclear distances and compared them with more accurate values given by Piszczatowski *et al.* [81] and by Stanke *et al.* [129] obtained with the explicitly correlated Gaussian wave functions. Our extrapolated results are given in Table II and compared with the two sets of reference values. One can see a reasonable agreement between the present results and Refs. [81,129]. The biggest absolute deviation from the values of Piszczatowski *et al.* [81] is about 4%. This is only slightly larger than for the helium atom. This error increase can be (at least partially) attributed to the fact that a larger d7Z basis set was used for the helium atom, while calculations for the hydrogen molecule were restricted to the d6Z basis.

Finally, in Table III, we show results of the calculations for the lithium and beryllium atoms as well as the corresponding cations. Our extrapolated values are compared with the reference data taken from the papers of Frolov *et al.* [128,130] and Pachucki *et al.* [131,132]. The errors are consistently within the range of 1–2%. Only for the lithium cation is the accuracy slightly worse (≈3%), but this is probably accidental. We can also check how well the relative differences are reproduced

TABLE III. Expectation values of the Araki-Sucher distribution for the lithium and beryllium atoms (Li, Be) and their cations (Li^+, Be^+). All values are given in atomic units.

Basis	$\langle \widehat{P}(r_{12}^{-3}) \rangle$			
	Li	Li^+	Be	Be^+
d3Z	−2.891	−2.924	−15.32	−15.38
d4Z	−2.194	−2.241	−13.52	−13.61
d5Z	−1.718	−1.774	−12.06	−12.18
d6Z	−1.397	−1.460	−11.25	−11.38
Extrapolation	+0.267	+0.173	−7.320	−7.505
Reference	+0.2734[a]	+0.1789[b]	−7.3267[c]	−7.5146[a]

[a]Reference [132].
[b]Reference [130].
[c]Reference [131].

TABLE IV. Expectation values of the Araki-Sucher distribution for the magnesium atom (Mg) and its cation (Mg^+), and the argon atom (Ar) and its dimer (Ar_2). All values are given in atomic units. The uncertainties in the final values are estimated to be about 5%.

Basis	$\langle \widehat{P}(r_{12}^{-3}) \rangle$			
	Mg	Mg^+	Ar	Ar_2
d2Z	−1371.3	−1370.5	−6090.3	−12179.9
d3Z	−1331.1	−1330.2	−6022.7	−12044.8
d4Z	−1315.9	−1315.0	−5963.4	−11926.1
d5Z	−1295.0	−1294.2	−5917.1	−11833.7
Extrapolation	−1220.7	−1221.4	−5440.8	−10881.0

in our method. To this end, we calculate contributions of the Araki-Sucher term to the ionization energies of the lithium and beryllium atoms and compare the results with Refs. [131,132]. In both cases, we find a remarkable agreement within approximately 1% of the total value.

To sum up, the method of calculating the Araki-Sucher correction proposed here is fundamentally valid and useful in practice. By comparing our results with the reference data available in the literature for several few-body systems, we conclude that it is capable of reaching an accuracy of a few percents or better. This is true provided that sufficiently large basis sets and accurate electronic structure methods are employed. Moreover, extrapolation to the complete basis-set limit must be performed in every case. The theoretically derived leading-order formula (70) is very efficient in this respect.

B. Results for many-electron systems

The biggest advantage of the method proposed here is that it can be applied to systems that are much larger than studied previously. This includes not only many-electron atoms, but also diatomic and even polyatomic molecules. To illustrate this, we performed calculations for several many-body systems: the magnesium atom (Mg) and its ion (Mg^+), and the argon atom (Ar) and its dimer (Ar_2). In the case of Mg and Mg^+, we employed the IP-EOM-CCSD-3A method [133,134] and the basis sets "aug-cc-pwCVX" reported in Ref. [127]. For the Ar and Ar_2 systems, we used the CCSD(T) method and the basis sets "disp-XZ+2/AE" developed by Patkowski and Szalewicz [135] specifically for the accurate description of the argon dimer. The results are shown in Table IV. Overall, the rate of convergence of the values obtained in finite basis sets is similar as that for the helium atom, which validates the extrapolation formula (70) for many-electron systems. We can estimate that the accuracy of the results shown in Table IV is not worse than 5%.

With the help of the results from Table IV, one can also calculate the contribution of the Araki-Sucher correction to the ionization energy of the magnesium atom and interaction energy of the argon dimer. The former quantity is approximately equal to $-0.02\ \mathrm{cm}^{-1}$ (the negative sign indicates that this correction decreases the ionization energy). While this value seems to be very small, we note that it is of the same order of magnitude as the present-day experimental uncertainty in the measurement of the ionization energy of the magnesium atom, $0.03\ \mathrm{cm}^{-1}$ [136–138]. For the argon dimer, we calculate that the contribution to the interaction energy of the Araki-Sucher term is equal to $0.02\ \mathrm{cm}^{-1}$. Again, this value has to be put into context. The total interaction energy of the argon dimer is approximately $99\ \mathrm{cm}^{-1}$. Therefore, while the Araki-Sucher contribution is small on the absolute scale, it becomes non-negligible in relation to other subtle effects. Moreover, the theoretical accuracy attainable for the argon dimer at present [135,139,140] is already quite close to the level where the QED effects come into play.

V. CONCLUSIONS

In the present work, we have put forward a general scheme to calculate the Araki-Sucher correction for many-electron systems. Several obstacles had to be removed to accomplish this goal. First, the complicated two-electron integrals involving the Araki-Sucher distribution have been solved with help of the McMurchie-Davidson technique (within the Gaussian-type orbitals basis set). It has been shown that they can be expressed through a family of one-dimensional integrals. Recursive and numerically stable computation of the latter integrals has been discussed in detail.

Second, the issue of convergence of the results with respect to the size of the basis set has been considered. We have demonstrated a slow convergence pattern ($\ln 2L/L$ in the leading order) towards the complete basis-set limit. This result has been verified by comparing with reference data for the helium atom. With the analytic information about the convergence at hand, extrapolations have been used to improve the accuracy of the results. The accuracy of about 1% has been achieved in this case.

To confirm the validity of the proposed approach, we have performed calculations for several few- and many-electron systems. First, we have concentrated on small systems (e.g., few-electron atoms, hydrogen molecule) for which accurate reference values are available in the literature. A consistent accuracy of a few percents has been obtained and the molecular results are only slightly less accurate than the atoms. Next, we have moved on to many-electron systems. We have estimated the contribution of the Araki-Sucher correction to the ionization energy of the magnesium atom and interaction energy of the argon dimer. The final values of the Araki-Sucher correction are comparable to the present-day experimental uncertainties of the measurements.

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APPENDIX: PARTIAL WAVE EXPANSION OF THE ARAKI-SUCHER DISTRIBUTION

In this Appendix, we present details of the derivation of Eqs. (49)–(54). Let us start with the definition (49) and split it into two parts, $\mathcal{A}_n(r_1,r_2;a) = \mathcal{A}_n^{(1)}(r_1,r_2;a) + \mathcal{A}_n^{(2)}(r_1,r_2;a)$, with

$$\mathcal{A}_n^{(1)}(r_1,r_2;a) = \frac{2n+1}{2}\int_0^\pi d\theta_{12}\, \sin\theta_{12} \times \frac{\theta(r_{12}-a)}{r_{12}^3} P_n(\cos\theta_{12}) \quad \text{(A1)}$$

and

$$\mathcal{A}_n^{(2)}(r_1,r_2;a) = 2\pi(2n+1)(\gamma+\ln a) \times \int_0^\pi d\theta_{12}\, \sin\theta_{12}\, \delta(\mathbf{r}_{12}) P_n(\cos\theta_{12}). \quad \text{(A2)}$$

The second of these integrals is straightforward to evaluate because, in the present context,

$$\delta(\mathbf{r}_{12}) = \frac{\delta(r_1-r_2)}{2\pi r_1^2}\frac{\delta(\theta_{12})}{\sin\theta_{12}}. \quad \text{(A3)}$$

Upon inserting back into Eq. (A2), the integration over the angle becomes straightforward and, with help of the expression $P_n(1)=1$, one arrives at

$$\mathcal{A}_n^{(2)}(r_1,r_2;a) = (2n+1)(\gamma+\ln a) r_1^{-2}\,\delta(r_1-r_2). \quad \text{(A4)}$$

Evaluation of the first term $\mathcal{A}_n^{(1)}(r_1,r_2;a)$ is much more complicated. Changing the integration variable in Eq. (A1) to $r_{12} = (r_1^2+r_2^2-2r_1r_2\cos\theta_{12})^{1/2}$ gives

$$\mathcal{A}_n(r_1,r_2;a) = \frac{2n+1}{2r_1r_2}\int_{|r_1-r_2|}^{r_1+r_2} dr_{12}\,\theta(r_{12}-a) \times \frac{1}{r_{12}^2} P_n\left(\frac{r_1^2+r_2^2-r_{12}^2}{2r_1r_2}\right). \quad \text{(A5)}$$

To get rid of the θ function under the integral sign, we need to distinguish three possible (and disjoint) cases. First, assuming that $a < |r_1-r_2|$, the integration range remains unchanged because $\theta(r_{12}-a)$ is equal to the unity there. The second case is $|r_1-r_2| < a < r_1+r_2$; the integrand vanishes whenever $r_{12} < a$ so that the lower integration limit has to be shifted to a. The third case is $a > r_1+r_2$; the result is zero because the integrand vanishes here. With this reasoning, the integral can be rewritten as

$$\mathcal{A}_n(r_1,r_2;a) = \theta(|r_1-r_2|-a)\frac{2n+1}{2} \times \int_{-1}^{+1} du\,\left(r_1^2+r_2^2-2r_1r_2u\right)^{-3/2} P_n(u)$$
$$+\,\theta(a-|r_1-r_2|)\theta(r_1+r_2-a)\frac{2n+1}{2} \times \int_{-1}^{u(a)} du\,\left(r_1^2+r_2^2-2r_1r_2u\right)^{-3/2} P_n(u) \quad \text{(A6)}$$

after the change of variables to $u = (r_1^2+r_2^2-r_{12}^2)/2r_1r_2$ and with the shorthand notation $u(a) = (r_1^2+r_2^2-a^2)/2r_1r_2$. The first integral is evaluated with elementary methods,

$$\int_{-1}^{+1} du\,\left(r_1^2+r_2^2-2r_1r_2u\right)^{-3/2} P_n(u) = \frac{2r_<^n r_>^{-n-1}}{(r_>-r_<)(r_>+r_<)}. \quad \text{(A7)}$$

The second integral is more complicated because of the function in the upper integration limit. It is probably quite difficult to derive the explicit expression for this integral, but fortunately we require only the leading-order term in a. The higher-order terms vanish in the final result due to the $a\to 0$ limit. To extract the leading-order contribution, we return to the original variable and integrate by parts once,

$$\int_{-1}^{u(a)} du\,\left(r_1^2+r_2^2-2r_1r_2u\right)^{-3/2} P_n(u) = \frac{1}{r_1r_2}\int_a^{r_1+r_2}\frac{dt}{t^2} P_n\left(\frac{r_1^2+r_2^2-t^2}{2r_1r_2}\right)$$
$$= -\frac{(-1)^n}{r_1r_2(r_1+r_2)} + \frac{1}{a}\frac{1}{r_1r_2} P_n\left(\frac{r_1^2+r_2^2-a^2}{2r_1r_2}\right) - \frac{1}{r_1^2r_2^2}\int_a^{r_1+r_2} dt\, P_n'\left(\frac{r_1^2+r_2^2-t^2}{2r_1r_2}\right). \quad \text{(A8)}$$

The first and the second terms are of the order of a^0 and a^{-1}, respectively. By integrating by parts again, one can show that the last term is also of the order of a^0. Therefore, we can write

$$\int_{-1}^{u(a)} du\,\left(r_1^2+r_2^2-2r_1r_2u\right)^{-3/2} P_n(u) = \frac{1}{a}\frac{1}{r_1r_2} P_n\left(\frac{r_1^2+r_2^2}{2r_1r_2}\right) + O(a^0), \quad \text{(A9)}$$

which is sufficient for the present purposes. Finally, to arrive at Eqs. (51)–(54) from the main text, one has to gather Eqs. (A4) and (A6)–(A9) and rearrange.

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