

Singular integrals and their application to a hypervirial theorem

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Hypervirial theorems provide relationships exact electronic wave functions must satisfy, and the extent to which this is the case is a measure (additional to the energy) of wave function quality. The hypervirial relation known as the Vinti equation has been proposed for this purpose, but its application has been hampered by the absence of analytical formulas for the singular integrals occurring therein. The authors' methods for singular integrals arising in atomic computations [J. Chem. Phys. **121**, 6323 (2004)] resolve this bottleneck; quality assessments based on the Vinti equation are provided here for a number of wave functions of varying complexity describing the He isoelectronic series (from H^- through Ne^{8+}).

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I. INTRODUCTION

Some of the relativistic and quantum electrodynamic (QED) corrections to the energies of helium-like and other three-body systems [1] involve matrix elements which, as usually written, are linear combinations of individually singular integrals that combine to yield a finite result. Similar behavior has been noted for the matrix elements of operators describing various electronic properties of these systems (see, for example, Thakkar and Smith [2]). Such convergent combinations of individually divergent integrals are referred to as Frullanian, commemorating a discussion by Frullani [3] of integrals of the form

$$\int_0^\infty \frac{f(at) - f(bt)}{t} dt = [f(\infty) - f(0)] \ln \frac{a}{b}. \quad (1)$$

A variety of methods have been employed [4] for reducing such combinations of integrals to their limiting values.

In a recent paper [5], we presented formulas for a number of “singular three-body integrals”—i.e. integrals of the generic form

$$I(\epsilon) = \int_\epsilon^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1-r_2|}^{r_1+r_2} f(r_1, r_2, r_{12}) dr_{12}, \quad (2)$$

where r_1 and r_2 are the distances of particles 1 and 2 from a third particle (in atomic systems, ordinarily the nucleus) and r_{12} is the distance between particles 1 and 2. These integrals are in fact regular for nonzero ϵ , but become singular (here meaning *divergent*) in the limit $\epsilon=0$. Since the $I(\epsilon)$ have now been reduced to algebraic form, Frullanian combinations of such integrals will lead to expressions in which the ϵ dependence vanishes in the limit $\epsilon=0^+$.

Our primary interest is in the use of basis functions which depend exponentially on all three interparticle distances r_1 , r_2 , and r_{12} (which we refer to collectively as r_i), in part because this symmetrical treatment of the three particles has distinct advantages for “nonadiabatic” systems (those in which all three particles are of comparable mass). We note that many of the observations made here have parallels in investigations based on Hylleraas wave functions (those with exponential dependence on r_1 and r_2 , but with r_{12} occurring only as powers). An extensive discussion of singular Hylleraas integrals has been given by Yan and Drake [6].

In the next section of this paper we define the exponential basis and identify the integrals arising in matrix elements based thereon. We then examine an application that naturally leads to Frullanian integrals: namely, the use of hypervirial theorems [7,8] in two-electron systems. Wave function quality can be assessed by comparing the expectation value of $(\mathbf{r}_1 \cdot \mathbf{r}_2)/r_1^3$ (normally written as a Frullanian sum of integrals) with the value predicted for it by the hypervirial formula known as the Vinti equation [9] (*vide infra*). Previous work along these lines has been hampered by the lack of an analytical expression for the Frullanian integrals, a lack which we have now resolved. We illustrate our present approach with a detailed investigation of the He isoelectronic series from $Z=1$ to 10. We examine the extent to which a variety of wave functions for these systems approach satisfaction of the Vinti equation in addition to their approach to accurate electronic energies.

II. DEFINITIONS

This communication deals with integrals arising from the use of basis functions of the form

$$\Psi_i = \mathcal{Y}_{LM,i}(\mathbf{r}_1, \mathbf{r}_2) \phi_i(r_1, r_2, r_{12}), \quad (3)$$

with

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$$\phi_i(r_1, r_2, r_{12}) = e^{-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_{12}}. \quad (4)$$

In these equations, \mathbf{r}_1 and \mathbf{r}_2 are vectors describing the positions of particles 1 and 2 relative to particle 3 and \mathcal{Y} is an angular eigenfunction of quantum numbers L, M (not necessarily the same function for each i ; for details see our earlier work [10,11]). The ϕ are “radial” functions, in the sense that they depend only on the magnitudes of the interparticle distances—i.e., on r_1, r_2 , and r_{12} . Of importance here is the fact that \mathcal{Y} contains powers of the interparticle distances of the form $r_1^{l_1} r_2^{l_2}$, with the sum $l_1 + l_2$ equal either to L or $L + 1$. The work cited above shows that for general operators the angular integrations can be carried out by standard methods, reducing the matrix elements of such operators to linear combinations of integrals in the interparticle coordinates. Similar reductions for Hylleraas wave functions (assuming that r_{12} is expanded in terms of \mathbf{r}_1 and \mathbf{r}_2 [12]) have been presented by Drake [13].

After the angular integrations have been performed, the expectation value of an operator M will be of the general form

$$\langle M \rangle = \sum_{ij} C_i^* C_j M_{ij}, \quad (5)$$

$$M_{ij} = \langle \phi_i | \bar{M} | \phi_j \rangle, \quad (6)$$

where C_i and C_j are coefficients that include normalization factors and \bar{M} is an operator which may involve the r_i and their derivatives. The application of \bar{M} to ϕ_j will leave its exponential form unaltered, but will cause it to be multiplied by a polynomial in the r_i and for some \bar{M} also multiplied by negative powers of one or more r_i .

If M_{ij} is expanded into monomial radial integrals, each will be of the form

$$\Gamma_{lmn}(a, b, c) = \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1 - r_2|}^{r_1 + r_2} dr_{12} r_1^l r_2^m r_{12}^n e^{-ar_1 - br_2 - cr_{12}}. \quad (7)$$

For matrix elements involving ϕ_i and ϕ_j , $a = \alpha_i + \alpha_j$, $b = \beta_i + \beta_j$, and $c = \gamma_i + \gamma_j$. The above formula is an optimum starting point for further analysis, but physical insight may be obtained by rewriting it as an integral over the space of the two vector coordinates \mathbf{r}_1 and \mathbf{r}_2 :

$$\Gamma_{lmn}(\alpha, \beta, \gamma) = \frac{1}{8\pi^2} \int d\mathbf{r}_1 d\mathbf{r}_2 r_1^{l-1} r_2^{m-1} |\mathbf{r}_1 - \mathbf{r}_2|^{n-1} \times e^{-\alpha r_1 - \beta r_2 - \gamma |\mathbf{r}_1 - \mathbf{r}_2|}. \quad (8)$$

Noting that the nonrelativistic Hamiltonian of a Coulombic system contains no r_i to any power smaller than -1 , we see from Eq. (8) that the matrix elements of the Hamiltonian will involve only Γ_{lmn} with $l, m, n \geq 0$, all of which are nonsingular. However, operators containing (or generating) higher negative powers of r_i will involve Γ_{lmn} with negative index values and therefore may lead to Frullanian combinations of the Γ_{lmn} .

As illustrated by our previous work [5], $\Gamma_{-1,m,n}$ and $\Gamma_{-1,-1,n}$ are nonsingular for $m, n \geq 0$, but Γ_{lmn} are singular if any of the indices are -2 or smaller. The integral $\Gamma_{-1,-1,-1}$ is also singular.

III. APPLICATION: HYPERVIRIAL THEOREM

As a practical application involving a Frullanian integral, we consider computations arising from the use of hypervirial theorems [7,8]. These theorems arise out of the general relationship, valid for an eigenstate Ψ of a Hamiltonian H and for an arbitrary operator A ,

$$\langle \Psi | \frac{dA}{dt} | \Psi \rangle = \langle \Psi | [H, A] | \Psi \rangle = 0. \quad (9)$$

By the use of various choices of A , one can obtain relationships among expectation values (*hypervirial theorems*) that will be satisfied only when the wave functions are exact eigenstates of H . These hypervirial theorems can be used to obtain expectation values that are difficult to calculate, expressing them in terms of others whose evaluation may be simpler. Alternatively, the extent to which hypervirial theorems are satisfied can be used as indicators of the quality of approximate wavefunctions.

For a nonrelativistic helium-like system consisting of an infinitely massive nucleus of charge Z and two electrons (particles 1 and 2), the choice $A = \mathbf{r}_1 \cdot \mathbf{p}_2 + \mathbf{r}_2 \cdot \mathbf{p}_1$, with \mathbf{p}_i the momentum operator for particle i , leads (using hartree atomic units $\hbar = e = m_e = 4\pi\epsilon_0 = 1$) to

$$\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle = Z \left\langle \frac{\mathbf{r}_1 \cdot \mathbf{r}_2}{r_1^3} \right\rangle + \frac{1}{2} \left\langle \frac{1}{r_{12}} \right\rangle, \quad (10)$$

a hypervirial theorem that was discussed by Vinti [9] and later used by Fischer and Smentek-Mielczarek [14] and by Kleinekathöfer, Patil, Tang, and Toennies [15] (KPTT). Our present interest is to study the rate at which Eq. (10) (which we shall call the Vinti equation) converges to validity as the wave functions of He-like ground states are improved. This study will require the evaluation of not only $\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle$ and $\langle r_{12}^{-1} \rangle$, both of which are straightforward, but also that of $\langle (\mathbf{r}_1 \cdot \mathbf{r}_2) / r_1^3 \rangle$, which by insertion of the formula

$$\mathbf{r}_1 \cdot \mathbf{r}_2 = \frac{1}{2} (r_1^2 + r_2^2 - r_{12}^2) \quad (11)$$

becomes

$$\left\langle \frac{\mathbf{r}_1 \cdot \mathbf{r}_2}{r_1^3} \right\rangle = \frac{1}{2} \left[\left\langle \frac{1}{r_1} \right\rangle + \left\langle \frac{r_2^2}{r_1^3} \right\rangle - \left\langle \frac{r_{12}^2}{r_1^3} \right\rangle \right]. \quad (12)$$

The matrix elements M_{ij} needed, in conjunction with Eq. (5), to evaluate the right-hand side of Eq. (12), can, with neglect of the prefactor $1/8\pi^2$ of Eq. (8), be written

TABLE I. Hypervirial computations on He. N is the number of symmetrized configurations in the wave function, E is the total energy (hartrees), and T and V are, respectively, the kinetic and potential energies. For $\langle(\mathbf{r}_1 \cdot \mathbf{r}_2)/r_1^3\rangle$, “Direct” is by Eq. (14) and (15); “Vinti” is by Eq. (10).

N	E (hartree)	$-\langle V \rangle / \langle T \rangle$	$\langle(\mathbf{r}_1 \cdot \mathbf{r}_2)/r_1^3\rangle$ (bohr $^{-1}$)	
			Direct	Vinti
1	-2.899 534 38	2.000 000	-0.201 091	-0.142 120
4	-2.903 688 26	2.000 000	-0.158 210	-0.157 023
10	-2.903 717 569 080 07	2.000 011 523 761 803	-0.157 022 614 765	-0.156 911 360 339
400	-2.903 724 377 034 05	2.000 000 000 000 125	-0.156 919 876 898	-0.156 919 874 660
500	-2.903 724 377 034 07	2.000 000 000 000 067	-0.156 919 873 963	-0.156 919 874 659
600	-2.903 724 377 034 09	2.000 000 000 000 207	-0.156 919 875 892	-0.156 919 874 658
700	-2.903 724 377 034 10	1.999 999 999 999 952	-0.156 919 874 730	-0.156 919 874 658
800	-2.903 724 377 034 11	2.000 000 000 000 042	-0.156 919 874 165	-0.156 919 874 658
∞^a	-2.903 724 377 034 12			

^aReference [19].

$$M_{ij} = \left\langle \phi_i \left| \frac{\mathbf{r}_1 \cdot \mathbf{r}_2}{r_1^3} \right| \phi_j \right\rangle$$

$$= \frac{1}{2} [\Gamma_{0,1,1}(a,b,c) + \Gamma_{-2,3,1}(a,b,c) - \Gamma_{-2,1,3}(a,b,c)],$$
(13)

with $a = \alpha_i + \alpha_j$, etc. The first of the three Γ is regular, being in fact that needed for $\langle r_1^{-1} \rangle$, but the other two are singular. Since M_{ij} is finite, it can be concluded that the two singular integrals constitute a Frullanian pair.

Using the formulas we recently published [5], we find, as discussed in more detail in the Appendix,

$$\Gamma_{-2,3,1}(a,b,c) - \Gamma_{-2,1,3}(a,b,c)$$

$$= \frac{192bc}{(b^2 - c^2)^4} \left[a \ln \left(\frac{a+b}{a+c} \right) - b + c \right]$$

$$+ \frac{48bc}{(b^2 - c^2)^3} \left[\frac{1}{a+b} + \frac{1}{a+c} \right]$$

$$- \frac{4}{(b^2 - c^2)^2} \left[\frac{b}{(a+c)^2} - \frac{c}{(a+b)^2} \right].$$
(14)

Equation (14) is regular, the singularities in the individual Γ having canceled, and is both efficient and numerically stable except when $b-c$ approaches zero. In that regime, it is better to use the alternate formula (also discussed in the Appendix)

$$\Gamma_{-2,3,1}(a,b,c) - \Gamma_{-2,1,3}(a,b,c)$$

$$= \frac{12(G_{-2,1,0} - G_{-2,0,1})}{(b+c)^4} + \frac{6(G_{-2,2,0} - G_{-2,0,2})}{(b+c)^3}$$

$$+ \frac{3(G_{-2,2,1} - G_{-2,1,2}) + G_{-2,3,0} - G_{-2,0,3}}{(b+c)^2}$$

$$+ \frac{G_{-2,3,1} - G_{-2,1,3}}{b+c}.$$
(15)

Here all the G have arguments a, b, c and are given by the general formula

$$G_{-p,m,n}(a,b,c) = \frac{2m!n!(m+n-p+1)!}{(m+n+1)!(a+b)^{n+m-p+2}}$$

$$\times {}_2F_1(n+1, m+n-p+2; m+n+2; \tau),$$
(16)

with $\tau = (b-c)/(a+b)$ and ${}_2F_1$ a hypergeometric function [16]. For the small τ for which Eq. (16) is to be used, the hypergeometric function is best evaluated from its series expansion, which corresponds (for the cases needed here) to the explicit formula

$$G_{-2,m,n}(a,b,c) = \frac{2m!}{(a+b)^{m+n}}$$

$$\times \sum_{\mu=0}^{\infty} \frac{(n+\mu)! \tau^\mu}{(m+n+\mu)(m+n+\mu+1)\mu!}.$$
(17)

IV. RESULTS AND DISCUSSION

Using Eqs. (14) and (15), we made an extensive study of the convergence of Eq. (10) toward validity for ground states of the He-like systems with Z from 1 to 10 (i.e., H^-, He, \dots, Ne^{8+}). Our study involved variationally determined wave functions with numbers (N) of symmetry-adapted configurations ranging from 1 to 800. For $N \leq 400$, the nonlinear parameters α_i , β_i , and γ_i were (except where stated otherwise) carefully (but not quite exhaustively) optimized; for larger values of N these parameters were chosen by the pseudorandom sampling technique introduced by Thakkar and Smith [2] and further developed by Frolov [17,18].

Data for He are presented in Table I. It is apparent that, with the exception of the ten-configuration results, the ratio

TABLE II. Comparative convergence of the energy and Vinti equation (indicated by “Vinti-Direct”) encountered while optimizing four-configuration calculations of the Li^+ ion. “Direct” is by Eq. (14) and (15); “Vinti” is by Eq. (10).

Energy	Direct	$\langle(\mathbf{r}_1 \cdot \mathbf{r}_2)/r_1^3\rangle$, bohr ⁻¹	
		Vinti	Vinti-Direct
-7.279 831 103	-0.166 005	-0.165 393	0.000 612
-7.279 834 641	-0.166 066	-0.165 320	0.000 746
-7.279 836 231	-0.165 856	-0.165 373	0.000 483
-7.279 913 413 ^a			0.000 000

^aExact energy [20].

$-\langle\text{potential energy}\rangle/\langle\text{kinetic energy}\rangle$ has essentially the exact value (2) predicted by the (ordinary) virial theorem. This is not a coincidence, because the uniform scaling of all the parameters of *any* wavefunction built from the exponential basis will produce an energy minimum at the scale which also satisfies the virial theorem. This observation, in turn, means that the degree of satisfaction of the virial theorem provides no information as to the quality of our wave functions other than their overall scale. All that can be said is that if the virial theorem is *not* well satisfied (cf. our ten-configuration result), one can conclude that the wave function is not optimized within the scope of the chosen parameter space.

Since hypervirial theorems provide additional relationships which are guaranteed to be satisfied only for exact wave functions, they have the potential of yielding additional

insight as to wave function quality. Returning to Table I, look now at the convergence of direct calculations of $\langle(\mathbf{r}_1 \cdot \mathbf{r}_2)/r_1^3\rangle$ toward values derived from the Vinti equation. Unlike the virial ratio, the Vinti equation is far from satisfied for relatively crude wave functions, and there is a strong correlation between its satisfaction and convergence of the wave function toward exactness. However, it must be pointed out that the convergence of the Vinti equation is a different measure than convergence of the energy; this point is illustrated by some data for Li^+ , which are presented in Table II, in which the entries are arranged in order of accuracy in the energy, but this ordering is not that of convergence to satisfaction of the Vinti equation. Finally, note that the additional criterion provided by the Vinti equation will have particular value in circumstances where (unlike the present example) it is impractical to carry computations to extreme precision, and a nearly exact wave function is not available.

A further examination of Table I indicates that, even for relatively crude wave functions, the Vinti equation gives more accurate results for $\langle(\mathbf{r}_1 \cdot \mathbf{r}_2)/r_1^3\rangle$ than are achieved by direct calculation of that quantity. In addition, both the table entries and data for other nonoptimum wave functions (not tabulated) indicate that the Vinti values are also more stable (with respect to small changes in the wave function) than are the direct values.

Table III provides information for additional members of the He isoelectronic series: H^- , Li^+ , N^{5+} , and Ne^{8+} . These systems show behavior similar to that already noted.

An extensive discussion of the Vinti equation as an indicator of wave function quality was provided by KPTT [15], who used it when studying the compact wave functions they

TABLE III. Hypervirial computations on ions isoelectronic with He. N is the number of symmetrized configurations in the wave function, and E is the total energy. For $\langle(\mathbf{r}_1 \cdot \mathbf{r}_2)/r_1^3\rangle$, “Direct” is by Eq. (14) and (15); “Vinti” is by Eq. (10).

	N	E (hartree)	$\langle(\mathbf{r}_1 \cdot \mathbf{r}_2)/r_1^3\rangle$ (bohr ⁻¹)	
			Direct	Vinti
H^-	1	-0.523 865 93	-0.196 415	-0.115 904
	4	-0.527 713 12	-0.127 667	-0.122 587
	400	-0.527 751 016 544 31	-0.122 630 969 740	-0.122 630 969 256
	∞^a	-0.527 751 016 544 38		
Li^+	1	-7.275 710 28	-0.206 073	-0.148 339
	4	-7.279 878 88	-0.165 748	-0.165 004
	400	-7.279 913 412 668 70	-0.164 961 334 466	-0.164 961 331 067
	∞^b	-7.279 913 412 669 31		
N^{5+}	1	-44.777 256	-0.211 664	-0.155 219
	4	-44.781 412	-0.173 972	-0.173 330
	400	-44.781 445 148 599	-0.173 362 096 282	-0.173 362 051 354
	∞^b	-44.781 445 148 773		
Ne^{8+}	1	-93.902 624	-0.212 975	-0.156 687
	4	-93.906 774	-0.175 774	-0.175 103
	400	-93.906 806 510 680	-0.175 153 963 503	-0.175 153 944 054
	∞^b	-93.906 806 515 037		

^aReference [21].

^bReference [20].

TABLE IV. Comparison of the compact wave functions of this research (of four symmetrized configurations) with those of KPTT [15]. The “Vinti” values of $2\langle\mathbf{p}_1 \cdot \mathbf{p}_2\rangle$ are calculated by evaluating the right-hand side of Eq. (10).

		$E - E_{\text{exact}}$ ($\mu\text{hartree}$)	$2\langle\mathbf{p}_1 \cdot \mathbf{p}_2\rangle$, hartree		
			Direct	Vinti	Exact ^a
H ⁻	KPTT ^b	2100	0.0628	0.0408	
	This work	38	0.0659	0.0558	0.0658
He	KPTT	3720	0.309	0.284	
	This work	36	0.318	0.313	0.318
Li ⁺	KPTT	5000	0.555	0.537	
	This work	35	0.578	0.572	0.578
Be ²⁺	KPTT	5700	0.852	0.813	
	This work	34	0.841	0.835	0.841

^aFrom our work (more accurate than the data given by KPTT).

^bWith a sign change (private communication from KPTT to V.H.S.).

introduced for He-like systems. The wave functions of the present study that are most similar in complexity to those of KPTT are those consisting of four optimized configurations, and we therefore give, in Table IV, some data comparing the two types of wave functions. Since KPTT used direct and Vinti-derived values of $2\langle\mathbf{p}_1 \cdot \mathbf{p}_2\rangle$ as an indicator [rather than those of $\langle(\mathbf{r}_1 \cdot \mathbf{r}_2)/r_1^3\rangle$, used in our Tables I–III], we have converted our data to make the comparison more straightforward. We have also changed the “exact” values of this quantity from those given by KPTT to more accurate values based on our most extensive configuration-interaction wave functions.

While the KPTT data have the conceptual advantage of having parameters determined from the short- and long-range behavior of the wave functions, with the main arbitrariness residing in the choice of its detailed functional form, we note that the compact four-configuration wave functions of the present study provide a significantly higher accuracy than the KPTT wave functions and with what appears to be a comparable, or perhaps smaller, degree of computational effort. The high quality of these four-configuration wave functions is attested not only by their energies but also by their satisfaction of the Vinti theorem and by the convergence of $2\langle\mathbf{p}_1 \cdot \mathbf{p}_2\rangle$ to its known accurate value. The improvement relative to KPTT in both these indicators approaches an order of magnitude.

The formulas of Eqs. (14) and (15) can also be used to check the data two of us (A.M.F. and V.H.S.) presented in a recent paper reporting highly accurate computations on He-like ions [20]. Values given as 14-figure estimates of $\langle(\mathbf{r}_1 \cdot \mathbf{r}_2)/r_1^3\rangle$, obtained using the Vinti equation, were listed in the last column of Table 4 of that paper. Those table entries do not agree with computations by the methods of the present paper, and the source of the discrepancy has been identified [22]. A recalculation of $\langle(\mathbf{r}_1 \cdot \mathbf{r}_2)/r_1^3\rangle$, using a corrected version of Eq. (36) of Ref. [20], is given here in Table V. We are confident that these data are correct because they are consistent with the convergence limits of the “Direct” and “Vinti” data presented in Tables I and III.

V. CONCLUDING REMARKS

The quantity $\langle\mathbf{p}_1 \cdot \mathbf{p}_2\rangle$ appears in a variety of contexts. It occurs in the description of isotopic mass shifts [14] (multiplied by the ratio of the electronic to the nuclear mass); it has also been used (divided by the expectation value of the kinetic energy) as an angular correlation coefficient of the particle momenta [23,24]. Krause, Morgan, and Berry [25] even used the Vinti equation as an aid to estimating the sign of $\langle\mathbf{p}_1 \cdot \mathbf{p}_2\rangle$ in low-lying states of two-electron atoms; they were, however, hampered by the unavailability of an explicit formula (such as has been presented here) for the integral $\langle(\mathbf{r}_1 \cdot \mathbf{r}_2)/r_1^3\rangle$.

The use of the Vinti equation to assess wave function quality will be of particular value in circumstances where highly accurate wave functions are needed. A case in point is the isotopic mass shift, where great sensitivity to the wave function has been observed [14,26]. The importance of this issue is illustrated by a current paper in which a combination of the mass shift with relevant relativistic and quantum electrodynamic corrections has been used in conjunction with

TABLE V. Values of $\langle(\mathbf{r}_1 \cdot \mathbf{r}_2)/r_1^3\rangle$ for He-like systems with nuclear charges Z from 1 to 10. These data are corrections of the entries in the last column of Table 4 of Ref. [20].

Z	$\langle(\mathbf{r}_1 \cdot \mathbf{r}_2)/r_1^3\rangle$, bohr ⁻¹
1	−0.122 630 969 255
2	−0.156 919 874 657
3	−0.164 961 331 058
4	−0.168 728 770 878
5	−0.170 919 078 378
6	−0.172 351 754 727
7	−0.173 362 048 943
8	−0.174 112 782 451
9	−0.174 692 605 007
10	−0.175 153 918 842

laser spectroscopic data to provide a model-independent experimental determination of nuclear radii [27].

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APPENDIX: EVALUATION OF $\Gamma_{-2,3,1}-\Gamma_{-2,1,3}$

The most straightforward way to proceed is to start from Eq. (22) of Ref. [5], which gives an explicit formula for $\Gamma_{-2,1,1}$:

$$\begin{aligned} \Gamma_{-2,1,1}(a,b,c) = & -4 \frac{\ln \epsilon + \gamma_E}{(b+c)^3} + \frac{4}{(b^2-c^2)^3} [(4abc + 3b^2c + c^3) \\ & \times \ln(a+b) - (4abc + 3bc^2 + b^3) \ln(a+c)] \\ & - \frac{16bc}{(b+c)^3(b-c)^2}. \end{aligned} \quad (\text{A1})$$

Here γ_E is Euler's constant, 0.57721.... Note that $\Gamma_{-2,1,1}$ is singular, as evidenced by its logarithmic dependence upon ϵ . It is apparent from Eq. (7) that the indices in Γ_{lmn} can be incremented by differentiation with respect to the parameters a , b , and c and that, specifically,

$$\Gamma_{-2,3,1}(a,b,c) - \Gamma_{-2,1,3}(a,b,c) = \left(\frac{\partial^2}{\partial b^2} - \frac{\partial^2}{\partial c^2} \right) \Gamma_{-2,1,1}(a,b,c). \quad (\text{A2})$$

Carrying out the process indicated in Eq. (A2), the singular terms, as expected, cancel, and we are left with the expression shown in Eq. (14) of the main text.

When $b-c$ is small, it is better to use the recursive process described by Eq. (24) of Ref. [5]; its key element is the formula of Sack, Roothaan, and Kolos [28]:

$$\begin{aligned} \Gamma_{l,m,n}(a,b,c) = & \left(\frac{1}{b+c} \right) [m\Gamma_{l,m-1,n}(a,b,c) + n\Gamma_{l,m,n-1}(a,b,c) \\ & + G_{l,m,n}(a,b,c)], \end{aligned} \quad (\text{A3})$$

in which G (for the parameter values of relevance here) has the explicit form given in the main text, in Eqs. (16) and (17).

Equation (A3) is used iteratively, starting from index values $l=m=n=0$. It is self-starting (in the sense that no initial Γ_{lmn} values from other sources are needed to initiate the process), because the term $m\Gamma_{l,m-1,n}$ is to be omitted when $m=0$, as is $n\Gamma_{l,m,n-1}$ when $n=0$.

For the index values needed here, one may therefore start from

$$\Gamma_{-2,0,0} = \frac{G_{-2,0,0}}{b+c}, \quad (\text{A4})$$

with Γ and G having arguments a , b , and c . We make therefrom

$$\Gamma_{-2,1,0} = \left(\frac{1}{b+c} \right) (\Gamma_{-2,0,0} + G_{-2,-1,0}) = \frac{G_{-2,0,0}}{(b+c)^2} + \frac{G_{-2,1,0}}{b+c} \quad (\text{A5})$$

and continue in a similar fashion until $\Gamma_{-2,3,1}$ and $\Gamma_{-2,1,3}$ are reached.

We now form the difference $\Gamma_{-2,3,1}-\Gamma_{-2,1,3}$, causing $G_{-2,0,0}$ (which is singular) to cancel, leaving only the regular terms comprising Eq. (15) of the main text.

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- [1] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer, Berlin, 1957).
 [2] A. J. Thakkar and V. H. Smith, Jr., Phys. Rev. A **14**, 1 (1977).
 [3] G. Frullani, Mem. Soc. Ital. Soc. **20**, 448 (1828).
 [4] D. Zwillinger, *Handbook of Integration* (Jones and Bartlett, New York, 1992), pp. 157–159.
 [5] F. E. Harris, A. M. Frolov, and V. H. Smith, Jr., J. Chem. Phys. **121**, 6323 (2004).
 [6] Z.-C. Yan and G. W. F. Drake, Can. J. Phys. **72**, 822 (1994).
 [7] J. O. Hirschfelder, J. Chem. Phys. **33**, 1762 (1960).
 [8] J. O. Hirschfelder and C. A. Coulson, J. Chem. Phys. **36**, 941 (1962).
 [9] J. P. Vinti, Phys. Rev. **58**, 882 (1940).
 [10] A. M. Frolov and V. H. Smith, Jr., Phys. Rev. A **53**, 3853 (1996).
 [11] F. E. Harris, Adv. Quantum Chem. **47**, 127 (2004).
 [12] R. A. Sack, J. Math. Phys. **5**, 245 (1964).
 [13] G. W. F. Drake, Phys. Rev. A **18**, 820 (1978).
 [14] C. F. Fischer and L. Smentek-Mielczarek, J. Phys. B **16**, 3479 (1983).
 [15] U. Kleinekathöfer, S. H. Patil, K. T. Tang, and J. P. Toennies, Phys. Rev. A **54**, 2840 (1996).
 [16] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1972).
 [17] A. M. Frolov, Phys. Rev. A **57**, 2436 (1998).
 [18] A. M. Frolov, Phys. Rev. E **64**, 036704 (2001).
 [19] C. Schwartz, J. Comput. Methods Sci. Eng. **4**, 13 (2004).
 [20] A. M. Frolov and V. H. Smith, Jr., J. Phys. B **37**, 2917 (2004). See also Ref. [22].
 [21] A. M. Frolov and V. H. Smith, Jr., J. Phys. B **36**, 4837 (2003).
 [22] A. M. Frolov and V. H. Smith, Jr., J. Phys. B **37**, 4037 (2004).
 [23] W. Kutzelnigg, G. Del Re, and G. Berthier, Phys. Rev. **172**, 49 (1968).
 [24] A. J. Thakkar and V. H. Smith, Jr., Phys. Rev. A **23**, 473 (1981).
 [25] J. L. Krause, J. D. Morgan III, and R. S. Berry, Phys. Rev. A **35**, 3189 (1987).
 [26] T. Koga and H. Matsuyama, J. Chem. Phys. **118**, 3936 (2003).
 [27] L.-B. Wang, P. Mueller, K. Bailey, G. W. F. Drake, J. P. Greene, D. Henderson, R. J. Holt, R. V. F. Janssens, C. L. Jiang, Z.-T. Lu, T. P. O'Connor, R. C. Pardo, K. E. Rehm, J. P. Schiffer, and X. D. Tang, Phys. Rev. Lett. **93**, 142501 (2004).
 [28] R. A. Sack, C. C. J. Roothaan, and W. Kolos, J. Math. Phys. **8**, 1093 (1967).