On the acceleration of the convergence of singular operators in Gaussian basis sets

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Abstract

Gaussian type wave functions do not reproduce the interparticle cusps which results in a slow convergence of the expectation values of the operators involved in calculations of the relativistic and QED energy corrections. Methods correcting this deficiency are the main topic discussed in this paper. Benchmark expectation values of the singular operators for several few-electron systems are presented.

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I. INTRODUCTION

The method of exponentially correlated Gaussian (ECG) wave functions provides means of obtaining very accurate solutions of the Schrödinger equation for small, few-electron atomic and molecular systems. In the last decade it was shown that the method is capable of supplying the most accurate variational estimations of the nonrelativistic energy of 2- to 4-electron systems [1–7]. Recently, the ECG wave functions proved useful in determining also relativistic and radiative corrections [1, 4, 8–11]. A precise determination of the corrections requires an access to high quality fully correlated wave functions. However, the expectation value of the energy is not the only factor determining the quality of the wave function. It is commonly known that the Gaussian type wave functions, apart from their advantages, have also some drawbacks which lower their usefulness in certain applications. These drawbacks are related to the Kato cusp condition which is not fulfilled by the Gaussian functions. The exception are wave functions with a linear correlation factor like the LECG function [12, 13]. Such wave functions are also employed in the family of the R12-methods based on the Kutzelnigg's idea [14, 15].

In this paper we shall concentrate on relativistic and QED energy corrections. The singular operators involved in these corrections are very demanding with respect to local properties of the wave function. In this case the Gaussian type wave functions exhibit a convergence which can hardly be recognized as satisfactory. The operators in mind are the one- and two-electron Dirac delta operators, $\delta(\boldsymbol{r})$, the relativistic kinetic energy operator ∇^4, and the distributional operator $P(1/r_{ij}^3)$ entering the QED energy correction. In this paper we describe two, in principle general, regularization methods which allow the convergence of the pertinent expectation values to be significantly improved. We propose to use the name *Drachmanization* for the first methodology as it was introduced by R. J. Drachman [16]. The other method, which is introduced here, is based on a suitable integral transform and an asymptotic formula for the resulting integrand. Referring to these methods we will use the abbreviations Dr and IT for Drachmanization and integral transform, respectively. We illustrate our approaches by one molecular (H_2) and three atomic (He, Li, and Be) cases using accurate ECG wave functions. The atomic units are used throughout the paper.

II. THE WAVE FUNCTION

The energies and wave functions of the studied systems were obtained by variationally solving the stationary Schrödinger equation $\hat{H}\Psi = E\Psi$ with the nonrelativistic clamped nuclei Hamiltonian

$$\begin{aligned}\hat{H} &= -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \\ &- \sum_{I=1}^{N}\sum_{i=1}^{n}\frac{Z_I}{|\boldsymbol{r}_i - \boldsymbol{R}_I|} + \sum_{I=1}^{N-1}\sum_{J=I+1}^{N}\frac{Z_I Z_J}{|\boldsymbol{R}_I - \boldsymbol{R}_J|},\end{aligned} \tag{1}$$

where $\boldsymbol{r}_i$ and $\boldsymbol{R}_I$ are, respectively, the electronic and nuclear coordinates, and Z_I are the nuclear charges. Our trial wave function was assumed in the form of a K-term linear expansion in an n-electron basis

$$\Psi(\boldsymbol{r}, \boldsymbol{\sigma}) = \hat{\mathcal{A}}\left(\Xi_{n,S,M_S}(\boldsymbol{\sigma})\,\hat{\mathcal{P}}\sum_{k=1}^{K} c_k\psi_k(\boldsymbol{r})\right), \tag{2}$$

where $\hat{\mathcal{A}}$ and $\hat{\mathcal{P}}$ are the permutation and spatial symmetry projectors, respectively, and $\Xi_{n,S,M_S}(\boldsymbol{\sigma})$ is an n-electron spin function with the spin quantum numbers S and M_S. As the n-electron spatial basis functions, ψ_k, we employed the exponentially correlated Gaussian (ECG) functions of Singer [17]

$$\psi_k(\boldsymbol{r}) = \exp\left[-\left(\boldsymbol{r} - \boldsymbol{s}_k\right)\boldsymbol{A}_k\left(\boldsymbol{r} - \boldsymbol{s}_k\right)^T\right], \tag{3}$$

where the superscript T denotes a vector transpose. The linear parameters, c_k, were determined by the inverse iteration method of solving the standard general symmetric eigenvalue problem. The nonlinear parameters, contained in the vectors $\boldsymbol{s}_k$ and the positive definite matrices $\boldsymbol{A}_k$, were found in an extensive variational optimization process. Detailed description of the ECG method including the optimization strategy employed may be found in [5, 18–21].

III. REGULARIZATION METHODS

A. Drachmanization (Dr)

The first regularization method is based on the idea described in 1981 by Drachman [16], who expressed the expectation value of $\delta(\boldsymbol{r}_{jk})$ in an equivalent form containing global operators, namely

$$4\pi \left\langle \Psi \left| \delta(\boldsymbol{r}_{jk}) \right| \Psi \right\rangle \;=\; 2 \left\langle \Psi \left| \frac{1}{r_{jk}} (E_\Psi - \hat{V}) \right| \Psi \right\rangle$$
$$- \sum_i \left\langle \boldsymbol{\nabla}_i \Psi \left| \frac{1}{r_{jk}} \right| \boldsymbol{\nabla}_i \Psi \right\rangle, \tag{4}$$

where $\hat{V}$ is the potential energy operator. Analogously we can reduce the singularity of the electron-nucleus Dirac delta operator

$$4\pi \left\langle \Psi \left| \delta(\boldsymbol{r}_{kI}) \right| \Psi \right\rangle \;=\; 4 \left\langle \Psi \left| \frac{1}{r_{kI}} (E_\Psi - \hat{V}) \right| \Psi \right\rangle$$
$$-2 \sum_i \left\langle \boldsymbol{\nabla}_i \Psi \left| \frac{1}{r_{kI}} \right| \boldsymbol{\nabla}_i \Psi \right\rangle . \tag{5}$$

In a similar way, the relativistic kinetic energy term can be evaluated using

$$\left\langle \Psi \left| \sum_i \nabla_i^4 \right| \Psi \right\rangle = 4 \left\langle \Psi \left| (E_\Psi - \hat{V})^2 \right| \Psi \right\rangle - 2 \sum_{i>j} \left\langle \nabla_i^2 \Psi \middle| \nabla_j^2 \Psi \right\rangle . \tag{6}$$

The QED energy correction contains a distribution P which is defined as the limit

$$\left\langle \phi \left| P\left(\frac{1}{r^3}\right) \right| \psi \right\rangle \equiv \tag{7}$$
$$\lim_{a\to 0} \int \phi^*(\boldsymbol{r})\, \psi(\boldsymbol{r}) \left[\frac{1}{r^3}\, \Theta(r-a) + 4\,\pi\, \delta(\boldsymbol{r})\, (\gamma + \ln a) \right] d\boldsymbol{r},$$

with Θ and γ being the step function and the Euler constant, respectively. In order to obtain a more regular expression for P we need to find a function for which ∇^2 gives $P(1/r_{jk}^3)$, namely

$$\nabla_j^2 \left(\frac{1 + \gamma + \ln r_{jk}}{r_{jk}} \right) = -P\left(\frac{1}{r_{jk}^3} \right) . \tag{8}$$

Next, we perform similar rearrangements as before and obtain

$$\left\langle \Psi \left| P\left(\frac{1}{r_{jk}^3}\right) \right| \Psi \right\rangle \;=\; \sum_i \left\langle \boldsymbol{\nabla}_i \Psi \left| \frac{\ln r_{jk}}{r_{jk}} \right| \boldsymbol{\nabla}_i \Psi \right\rangle \tag{9}$$
$$+ \left\langle \Psi \left| 4\pi (1+\gamma)\, \delta(\boldsymbol{r}_{jk}) + 2\, (E_\Psi - \hat{V})\, \frac{\ln r_{jk}}{r_{jk}} \right| \Psi \right\rangle.$$

As can be seen, except $\delta(\boldsymbol{r}_{jk})$, which can be handled according to Eq. (4), singular operators are no longer present on the right-hand side of the equation above, but instead new types of integrals appear. In the ECG basis these integrals can be evaluated by means of elementary and the Clausen Cl_2 [22] functions, for example

$$\int e^{-a_1 r_1^2 - a_2 r_2^2 - a_3 r_{12}^2} \frac{\ln r_1}{r_1\, r_2}\, d\boldsymbol{r} \;=\; -\frac{2\,\pi^2}{a\, a_3}\, \left[\mathrm{Cl}_2(\pi + 2\, b) + b\, c \right], \tag{10}$$

where

$$
\begin{aligned}
a &= \sqrt{a_1\,a_2 + a_1\,a_3 + a_2\,a_3}\,, \\
b &= \arctan\left(\frac{a_3}{a}\right)\,, \\
c &= \gamma + \ln\left(\frac{4\,a^2}{a_2 + a_3}\right)\,.
\end{aligned}
\tag{11}
$$

The methodology described above is an extension of the original Drachman's idea to a couple of new operators, therefore, we dare to call this approach Drachmanization. The formulas (4), (5), (6), and (9) are general but an analytic evaluation of the right hand side integrals in the ECG basis is possible only for atoms. This prompted us to search for another method which, while preserving the accuracy, would be equally effective for atoms and molecules.

B. Integral transform (IT)

The idea of the IT approach is to move the singularity out of an expectation value to the new integral, and to derive the correct asymptotic formula for the integrand from the analytic behavior of the exact solution of the Schrödinger equation. This is the simplest approach, which can be applied to atoms as well as to molecules.

1. $\langle\Psi\,|\delta(\boldsymbol{r})|\,\Psi\rangle$

For the Dirac delta operators this method works as follows. One uses the Poisson equation

$$
\nabla^2\left(\frac{1}{r}\right) = -4\pi\delta(\boldsymbol{r}),
\tag{12}
$$

and replaces $1/r$ by an integral with the Gaussian function

$$
\frac{1}{r} = \frac{2}{\sqrt{\pi}}\int_0^\infty e^{-r^2t^2}\,dt.
\tag{13}
$$

This combination leads to the following integral form of the Dirac delta function

$$
\langle\Psi\,|\delta(\boldsymbol{r})|\,\Psi\rangle = \frac{1}{2\pi^{3/2}}\int_0^\infty \left\langle\Psi\left|2t^2\left(3-2t^2r^2\right)e^{-t^2r^2}\right|\Psi\right\rangle dt.
\tag{14}
$$

In a well optimized ECG basis set the matrix element of $e^{-t^2\,r^2}$ is highly accurate, provided that t is not very large, i.e., $t < t_\Lambda$. Therefore, the integral over $t > t_\Lambda$ is evaluated using an analytically derived asymptotic formula. This formula results from the Kato cusp condition which is fulfilled by the exact solution of the Schrödinger equation with Coulomb interactions. If one denotes by $f(t)$ the integrand in Eq. (14), then for large t we use the expansion

$$f(t) = \frac{4Z}{\sqrt{\pi}\,t^2}\,\langle\Psi\,|\delta(\boldsymbol{r})|\,\Psi\rangle\left(1+\frac{A_1}{t}+\frac{A_2}{t^2}+\frac{A_3}{t^3}+\cdots\right), \tag{15}$$

where A_i depend on the state under consideration, Ψ, and are obtained by fitting to a large grid of points of $f(t)$. For the electron-nucleus Dirac delta, Z is the nuclear charge whereas for the interelectron delta, $Z = -\frac{1}{2}$. It remains to make a proper choice of the value for t_Λ, which depends on the numerical accuracy of $f(t)$. This accuracy is estimated by calculating $f(t)$ for several lengths of basis sets and we found that most precise results with our wave functions are obtained with $t_\Lambda \approx 100$. In performing the integration in Eq. (14) one, at first, neglects the asymptotic formula, obtains approximate value for the Dirac delta, and in the next step uses it for the calculation of the integral over the asymptotic region. The result converges quickly with only a few iterations.

2. $\langle\Psi\,|P(1/r^3)|\,\Psi\rangle$

A similar approach can be applied to the calculation of the Araki-Sucher term, which is defined in Eq. (7). One transforms this term with the help of

$$-\frac{\ln r+\gamma}{r^2} = \int_0^\infty t\,(2\,\ln t-\gamma)\,e^{-t^2r^2}\,dt \tag{16}$$

and of the integration by parts to the following form

$$\begin{aligned}\int P\Big(\frac{1}{r_{ij}^3}\Big)\Psi^2(\boldsymbol{r})\,d\boldsymbol{r} \;&=\; -\int \frac{\ln r_{ij}+\gamma}{r_{ij}^2}\frac{\partial}{\partial r_{ij}}\Psi^2(\boldsymbol{r})\,d\boldsymbol{r}\\ &=\; \int_0^\infty (2\,\ln t-\gamma)\,f(t)\,dt\,,\end{aligned} \tag{17}$$

where

$$f(t) = \int 2t\Big(t^2 r_{ij}-\frac{1}{r_{ij}}\Big)e^{-t^2r_{ij}^2}\,\Psi^2(\boldsymbol{r})\,d\boldsymbol{r}\,. \tag{18}$$

As in the case of the Dirac delta function, the integral with $t < t_\Lambda$ is calculated directly with $f(t)$, while for $t > t_\Lambda$ one applies the asymptotic expansion

$$f(t) = \frac{\pi^{3/2}}{2\,t^2}\,\langle\Psi\,|\delta(\boldsymbol{r}_{ij})|\,\Psi\rangle\left(1+\frac{A_1}{t}+\frac{A_2}{t^2}+\frac{A_3}{t^3}+\cdots\right) \tag{19}$$

and calculates A_i by fitting to $f(t)$. The value of t_Λ is chosen as equal to that in the corresponding calculation of the Dirac delta.

3. $\langle \Psi | \nabla^4 | \Psi \rangle$

A different approach is applied in the case of $\langle \Psi | \nabla_1^4 | \Psi \rangle = \langle \Psi | p_1^4 | \Psi \rangle$. We switch to the momentum representation and calculate the one-electron momentum density function, $I(p_1)$, employing the Fourier transform of the coordinate wave function

$$\tilde{\Psi}(\boldsymbol{p}, \boldsymbol{\sigma}) = \int \Psi(\boldsymbol{r}, \boldsymbol{\sigma}) e^{-i\boldsymbol{p}\boldsymbol{r}}\, d\boldsymbol{r}\,. \tag{20}$$

We note in passing that the Fourier transform of the ECG basis function of Eq. (3),

$$\tilde{\psi}_k(\boldsymbol{p}) = |\tilde{\boldsymbol{A}}_k|^{-\frac{3}{2}} \exp\Big[-(\boldsymbol{p} - \tilde{\boldsymbol{s}}_k)\, \tilde{\boldsymbol{A}}_k\, (\boldsymbol{p} - \tilde{\boldsymbol{s}}_k)^T + \tilde{C}\Big] \tag{21}$$

with $\tilde{\boldsymbol{s}}_k = -2i\boldsymbol{s}_k\boldsymbol{A}_k$, $\tilde{\boldsymbol{A}}_k = \frac{1}{4}\boldsymbol{A}_k^{-1}$, and $\tilde{C} = -\boldsymbol{s}_k\boldsymbol{A}_k\boldsymbol{s}_k^T$, preserves the shape and all the advantages of the original ECG function, which enables the evaluation of integrals in the momentum space to be readily accomplished [7, 23]. The integration with respect to all the momenta but p_1 leads to

$$\left\langle \Psi \left| \sum_i p_i^4 \right| \Psi \right\rangle = n \int p_1^4\, \tilde{\Psi}(\boldsymbol{p})\, \tilde{\Psi}^*(\boldsymbol{p})\, d\boldsymbol{p} = \int_0^\infty p_1^4\, I(p_1)\, dp_1\,, \tag{22}$$

where

$$I(p) = 4\pi\, n\, p^2 \int \tilde{\Psi}(\boldsymbol{p}, \boldsymbol{p}_2, \ldots, \boldsymbol{p}_n)\, \tilde{\Psi}^*(\boldsymbol{p}, \boldsymbol{p}_2, \ldots, \boldsymbol{p}_n) \prod_{i=2}^{n} d\boldsymbol{p}_i\,. \tag{23}$$

The density function $I(p)$, as obtained from Gaussian geminals, is accurate for not too large values of the momentum. Therefore, the last integral in the equation above is evaluated directly for $p < p_\Lambda$ whereas for $p > p_\Lambda$ we use a large-p asymptotic expansion. This expansion can be obtained as follows. The large momentum behavior is related to small r in the coordinate representation. For example, for hydrogenic states

$$I(p) = \frac{32}{p^6} Z^2\, \langle \Psi | \delta(\boldsymbol{r}) | \Psi \rangle + O(p^{-8}). \tag{24}$$

The generalization to arbitrary (but nonrelativistic) atoms with n electrons is

$$I(p) = \frac{32}{p^6} \sum_{i=1}^{n} \Big(Z^2\, \langle \Psi | \delta(\boldsymbol{r}_i) | \Psi \rangle + \frac{1}{2} \sum_{j>i}^{n} \langle \Psi | \delta(\boldsymbol{r}_{ij}) | \Psi \rangle \Big) + O(p^{-8})\,, \tag{25}$$

which will be proven below. The result for molecules is more complicated and involves an oscillatory term of the order of p^{-7}. Let us present more detailed derivation for the diatomic molecule AB consisting of two-electrons. The generalization to arbitrary molecule will be obvious. The wave function is $\Psi = \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2)$. We perform the Fourier transform in the variable $\boldsymbol{r}_1$, while keeping $\boldsymbol{r}_2$ intact,

$$\tilde{\Psi}(\boldsymbol{p}_1, \boldsymbol{r}_2) = \int \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2)\, e^{-i\,\boldsymbol{p}_1\,\boldsymbol{r}_1}\, d\boldsymbol{r}_1\,. \tag{26}$$

The large $\boldsymbol{p}_1$ asymptotics is related to the cusps at both nuclei and at the other electron

$$\begin{aligned}\tilde{\Psi}(\boldsymbol{p}_1, \boldsymbol{r}_2) \;\approx\; & \frac{8\,\pi\,Z_A}{p_1^4}\,\Psi(\boldsymbol{R}_A, \boldsymbol{r}_2)\, e^{-i\,\boldsymbol{p}_1\,\boldsymbol{R}_A} + \frac{8\,\pi\,Z_B}{p_1^4}\,\Psi(\boldsymbol{R}_B, \boldsymbol{r}_2)\, e^{-i\,\boldsymbol{p}_1\,\boldsymbol{R}_B} \\ & -\frac{1}{2}\,\frac{8\,\pi}{p_1^4}\,\Psi(\boldsymbol{r}_2, \boldsymbol{r}_2)\, e^{-i\,\boldsymbol{p}_1\,\boldsymbol{r}_2}.\end{aligned} \tag{27}$$

The momentum density $I(\boldsymbol{p})$ is then $(n = 2)$

$$\begin{aligned} I(\boldsymbol{p}) \;=\; & n\,\frac{4\,\pi\,p^2}{(2\,\pi)^3}\int \tilde{\Psi}^*(\boldsymbol{p}, \boldsymbol{r}_2)\,\tilde{\Psi}(\boldsymbol{p}, \boldsymbol{r}_2)\, d\boldsymbol{r}_2 \\ \approx\; & n\frac{32}{p^6}\int\Big[Z_A\,\Psi(\boldsymbol{R}_A, \boldsymbol{r}_2)\, e^{-i\,\boldsymbol{p}\boldsymbol{R}_A} + Z_B\,\Psi(\boldsymbol{R}_B, \boldsymbol{r}_2)\, e^{-i\,\boldsymbol{p}\boldsymbol{R}_B} - \frac{1}{2}\,\Psi(\boldsymbol{r}_2, \boldsymbol{r}_2)\, e^{-i\,\boldsymbol{p}\boldsymbol{r}_2}\Big]^* \\ & \times\Big[Z_A\,\Psi(\boldsymbol{R}_A, \boldsymbol{r}_2)\, e^{-i\,\boldsymbol{p}\boldsymbol{R}_A} + Z_B\,\Psi(\boldsymbol{R}_B, \boldsymbol{r}_2)\, e^{-i\,\boldsymbol{p}\boldsymbol{R}_B} - \frac{1}{2}\,\Psi(\boldsymbol{r}_2, \boldsymbol{r}_2)\, e^{-i\,\boldsymbol{p}\boldsymbol{r}_2}\Big]\, d\boldsymbol{r}_2\,.\end{aligned} \tag{28}$$

After expanding the product of two square brackets, the mixing terms with $e^{-i\,\boldsymbol{p}\boldsymbol{R}_X}\, e^{-i\,\boldsymbol{p}\boldsymbol{r}_2}$ do not contribute to the large p asymptotics because of the integration over $\boldsymbol{r}_2$,

$$\begin{aligned} I(\boldsymbol{p}) \;=\; & n\,\frac{32}{p^6}\int\Big[Z_A^2\,\Psi^2(\boldsymbol{R}_A, \boldsymbol{r}_2) + Z_B^2\,\Psi^2(\boldsymbol{R}_B, \boldsymbol{r}_2) + \frac{1}{4}\,\Psi^2(\boldsymbol{r}_2, \boldsymbol{r}_2) \\ & + 2Z_A\,Z_B\,\cos\Big(\boldsymbol{p}(\boldsymbol{R}_A - \boldsymbol{R}_B)\Big)\Psi(\boldsymbol{R}_A, \boldsymbol{r}_2)\,\Psi(\boldsymbol{R}_B, \boldsymbol{r}_2)\Big]\, d\boldsymbol{r}_2 + O(p^{-8})\,.\end{aligned} \tag{29}$$

One averages with respect to all orientations of $\boldsymbol{p}$ relative to $\boldsymbol{R}_A - \boldsymbol{R}_B$ and obtains

$$\begin{aligned} I(p) \;=\; & n\,\frac{32}{p^6}\Big[Z_A^2\,\langle\Psi\,|\delta(\boldsymbol{r}_1 - \boldsymbol{R}_A)|\,\Psi\rangle + Z_B^2\,\langle\Psi\,|\delta(\boldsymbol{r}_1 - \boldsymbol{R}_B)|\,\Psi\rangle + \frac{1}{4}\,\langle\Psi\,|\delta(\boldsymbol{r}_1 - \boldsymbol{r}_2)|\,\Psi\rangle \\ & + Z_A\,Z_B\,\frac{2\,\sin(p\,|\boldsymbol{R}_A - \boldsymbol{R}_B|)}{p\,|\boldsymbol{R}_A - \boldsymbol{R}_B|}\int\Psi^*(\boldsymbol{R}_A, \boldsymbol{r}_2)\,\Psi(\boldsymbol{R}_B, \boldsymbol{r}_2)\;d\boldsymbol{r}_2\Big] + O(p^{-8})\,.\end{aligned} \tag{30}$$

For arbitrary diatomic molecules AB of the Σ symmetry, the large momentum behavior of the angularly averaged $I(p)$ is

$$\begin{aligned} I(p) \;=\; & \frac{32}{p^6}\sum_{i=1}^{n}\Big(Z_A^2\,\langle\Psi\,|\delta(\boldsymbol{r}_i - \boldsymbol{R}_A)|\,\Psi\rangle + Z_B^2\,\langle\Psi\,|\delta(\boldsymbol{r}_i - \boldsymbol{R}_B)|\,\Psi\rangle + \frac{1}{2}\sum_{j>i}^{n}\langle\Psi\,|\delta(\boldsymbol{r}_{ij})|\,\Psi\rangle\Big) \\ & + \frac{32}{p^6}\,Z_A Z_B\frac{2\sin(p\,|\boldsymbol{R}_A - \boldsymbol{R}_B|)}{p\,|\boldsymbol{R}_A - \boldsymbol{R}_B|}\sum_{i=1}^{n}\rho_i(|\boldsymbol{R}_A - \boldsymbol{R}_B|) + O(p^{-8})\,,\end{aligned} \tag{31}$$

where

$$\rho_1(|\boldsymbol{R}_A - \boldsymbol{R}_B|) = \int\Psi^*(\boldsymbol{R}_A, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_n)\,\Psi(\boldsymbol{R}_B, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_n)\prod_{i=2}^{n} d\boldsymbol{r}_i\,. \tag{32}$$

The higher order terms in the expansion (31) are obtained by fitting to $I(p)$ and the whole expansion is integrated analytically for $p > p_\Lambda$. The parameter p_Λ is selected differently for each system as it depends on the quality of the wave function but, in a wide range of its choice, has no influence on the final result.

IV. RESULTS AND DISCUSSION

The methodology described above was applied to three atomic (He, Li, Be) and one molecular (H_2) system. For their ground states accurate ECG wave functions are available from our previous papers (see Table I for details). Table I lists energy and its estimated accuracy corresponding to the largest expansion used for each out of the four systems.

The regularization methods were tested first on the helium atom case (Tab. II). For this system very accurate reference results, obtained from specialized exponential wave functions, are available [24–26]. The direct and Dr values of $\langle\delta(\boldsymbol{r}_{ij})\rangle$ were already published in [9], but are repeated here for the sake of completeness. Let us first note that the Dirac delta expectation value obtained in the direct ECG computation converges rather slowly, so that from the 600-term expansion merely 4 significant figures of the exact value can be recovered despite the fact that the same wave function gives 11 figures of the exact energy. Both types of regularization allow us to get another 4 significant digits. A similar observation can be made for $\langle p_i^4\rangle$ but this time the IT approach is more effective and yields 9 significant figures of the exact value. The expectation value of $P\left(1/r_{ij}^3\right)$ is particularly slowly convergent and in direct computations only 2 significant digits are obtained. The convergence is dramatically improved after the application of any of the two regularization methods so that an accuracy of 6 decimals is reached.

In Table III the expectation values for the lithium atom computed directly from the 2000-term ECG wave function and by means of the regularization methods are confronted with the very accurate results obtained by Yan and Drake from an exponential wave function [27]. In this case the direct computations give only 3 significant figures for the Dirac deltas and $\langle p_i^4\rangle$ and just the leading figure for $\left\langle P\left(1/r_{ij}^3\right)\right\rangle$. We gain several more decimal digits from the regularized calculations. In the case of lithium the IT approach seems to be consistently superior to the Drachmanization, with an exception of the latter operator, where both techniques seem to perform approximately equally well but the precise comparison is impossible due to the uncertainty of the reference value.

The largest atomic system considered is the beryllium. For Be there are no reference values of an accuracy comparable to that of He and Li, therefore, the precision of the computed expectation values can be assessed merely by inspecting the convergence patterns in Table IV. The effectiveness of Dr and IT methods reminds of that from the lithium atom calculation—the regularization enables the stabilization of at least 2 additional digits. We also present our recommended values estimated by an extrapolation to the infinite basis, using data combined from Dr and IT sequences. Our result $\langle\delta(\boldsymbol{r}_i)\rangle = 35.369\,5(5)$ agrees very well with 35.370 0 and 35.369 5 derived from the CI wave function expanded in Slater-type orbitals obtained by Bunge [28] and Esquivel and Bunge [29], respectively.

Within the Dr approach, computing the necessary molecular matrix elements involves a numerical integration. For H_2, therefore, we concentrated on the IT method which is more convenient to apply and our analysis of the convergence is based on the IT results given in Tab. V. The general observations are similar to that for atoms. Despite employing energetically extremely accurate wave functions (the 1200-term ECG function yields energy with an accuracy of a fraction of nanohartree), the direct computation yields only 3 significant digits for the Dirac deltas, 4 digits in case of $\langle p_i^4\rangle$, and just 2 for $\left\langle P\left(1/r_{ij}^3\right)\right\rangle$. As we can see from the last column of the table, the regularization allows the next 3 significant figures to be recovered. Our recommended values of $\langle\delta(\boldsymbol{r}_{iI})\rangle = 0.459\,668\,2(1)$ and $\langle\delta(\boldsymbol{r}_{ij})\rangle = 0.016\,743\,4(2)$ can be confronted with 0.459 663 and 0.016 774 0, respectively, computed by Wolniewicz from his 279-term explicitly correlated wave function of the Kołos-Wolniewicz type [30].

For molecules, the expectation value of p^4 requires a slightly different treatment than for atoms. The molecular asymptotic formula, Eq. (31), unlike for atoms, involves an oscillatory term of the order of p^{-7}. The amplitude of the oscillation is determined by a new quantity, $\rho = \sum_i \rho_i(|\boldsymbol{R}_A - \boldsymbol{R}_B|)$, defined in Eq. (32) and related to a nondiagonal one-electron density matrix. In Table VI we show the convergence and the extrapolated value of ρ for the hydrogen molecule at R=1.4. Note that for $\boldsymbol{R}_A = \boldsymbol{R}_B$, ρ reduces to $\langle\delta(\boldsymbol{r}_{iI})\rangle$, therefore, at small arguments ρ has numerical values close to that of $\langle\delta(\boldsymbol{r}_{iI})\rangle$. This relation can be illustrated by comparing our recommended value of $\rho = 0.444\,04(2)$ with the density at the nucleus equal to 0.459 668 2(1). Modeling the large-p momentum density using Eq. (31) enables the precision of $\langle p_i^4\rangle$ to be extended by additional 3 digits in comparison with the direct evaluation (see Tab. V).

To our knowledge, there are no published attempts to compute the Araki-Sucher term (7) for H_2. This term, together with the Bethe logarithm, is indispensable for a precise determination of the radiative energy correction of the order of α^3. In Tab. V we present the convergence of $\left\langle P\left(1/r_{ij}^3\right)\right\rangle$ obtained from both direct and IT computations, as well as our recommended value of 0.397 95(5).

The integral transform can also be used when the molecular wave function happens to be not very accurate or for not too short internuclear distances. Then the A_i coefficients can be taken from the corresponding atomic systems. We have checked such an approach for the hydrogen molecule and we claim that, even for such a small internuclear distance as $R = 1.4$, the atomic values of A_i can be used, without loosing much accuracy, if $t_\Lambda \gtrsim 100$.

V. SUMMARY

The main deficiency of any wave function expanded in a Gaussian basis is the lack of the cusps which results in a relatively slow convergence of expectation values of singular operators. On a few examples we have shown that this deficiency can be significantly weakened using a properly defined regularization. The new formulas for Drachmanized expectation values of singular operators enable acceleration of the convergence in the case of atoms. For molecules, however, this approach requires a numerical integration and therefore becomes less practical. The integral transform of the expectation values in connection with the corrected asymptotic expansion turns out to be a convenient alternative, at least equally efficient in most cases and with a clear advantage of being easily applicable to atoms and to molecules. Both methods lead to results 2-4 orders of magnitude more accurate, than those computed directly. Although we employed in our calculations the exponentially correlated Gaussian functions to generate benchmark results, the techniques presented in this work are, obviously, more general and can be used with any Gaussian basis. This opens a possibility of very accurate calculations of relativistic and QED effects using standard and well-established basis sets.

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TABLE I: The nonrelativistic energy, E, its relative error, ΔE, and the largest expansion length, K, of the ECG wave function applied.

System	K	$E/\mathrm{E_H}$	$\Delta E/\mathrm{E_H}$	Reference
He	600	$-2.903\,724\,377\,022$	$4.1 \cdot 10^{-12}$	[1]
Li	2000	$-7.478\,060\,315$	$1.2 \cdot 10^{-9}$	[10]
Be	1600	$-14.667\,355\,536$	$3.1 \cdot 10^{-8}$	[31]
H_2	1200	$-1.174\,475\,714\,037$	$1.6 \cdot 10^{-10}$	[1]

TABLE II: Helium atom. Convergence of the expectation values computed directly, using the Drachmanization (Dr), and by the integral transform (IT). An implicit summation over all the electrons and electron pairs is assumed in the notation used in this and the following tables.

K	Direct	Dr	IT
		$\langle\delta(\boldsymbol{r}_i)\rangle$	
75	3.608 216 79	3.620 805 82	3.620 610 00
150	3.617 782 37	3.620 856 06	3.620 854 50
300	3.619 595 30	3.620 858 21	3.620 858 39
600	3.620 611 21	3.620 858 62	3.620 858 63
'Exact' [24]		3.620 858 637 7(3)	
		$\langle\delta(\boldsymbol{r}_{ij})\rangle$	
75	0.106 951 650	0.106 341 763	0.106 414 468
150	0.106 465 966	0.106 345 233	0.106 346 293
300	0.106 378 464	0.106 345 356	0.106 345 437
600	0.106 358 176	0.106 345 369	0.106 345 383
'Exact' [25]		0.106 345 370 636(2)	
		$\langle p_i^4\rangle$	
75	107.849 86	108.181 61	108.173 524
150	108.097 26	108.177 55	108.176 048
300	108.143 96	108.176 53	108.176 115
600	108.169 77	108.176 29	108.176 135
'Exact' [24]		108.176 134 4(8)	
		$\left\langle P\left(1/r_{ij}^3\right)\right\rangle$	
75	0.948 422 0	0.989 485 6	0.978 295 5
150	0.978 706 2	0.989 284 5	0.989 120 0
300	0.985 876 4	0.989 274 8	0.989 261 8
600	0.987 804 9	0.989 273 5	0.989 272 1
'Exact' [26]		0.989 272 4(13)	

TABLE III: Lithium atom. Expectation values computed from the 2000-term ECG wave function by means of three methods: directly, using the Drachmanization (Dr), and by the integral transform (IT) in comparison with accurate Yan and Drake values [27].

	$\langle\delta(\boldsymbol{r}_j)\rangle$	$\langle\delta(\boldsymbol{r}_{ij})\rangle$	$\langle p_i^4\rangle$	$\left\langle P\left(1/r_{ij}^3\right)\right\rangle$
Direct	13.835 0	0.544 669	628.157	0.241 0
Dr	13.842 606 23	0.544 324 4	628.453 1	0.273 54
IT	13.842 609 63	0.544 326 6	628.449 0	0.273 37
[27]	13.842 609 642(55)	0.544 329 79(31)	628.449 144(5)	0.273 67(26)

TABLE IV: Beryllium atom. Convergence of the expectation values computed directly, using the Drachmanization (Dr), and by the integral transform (IT).

K	Direct	Dr	IT
		$\langle \delta(\boldsymbol{r}_i) \rangle$	
100	33.379 145	35.174 770	35.324 216
200	34.897 648	35.339 657	35.362 596
400	35.029 311	35.340 791	35.365 872
800	35.297 307	35.368 099	35.368 676
1600	35.317 352	35.368 900	35.368 880
∞		35.369 5(5)	
		$\langle \delta(\boldsymbol{r}_{ij}) \rangle$	
100	1.627 741	1.604 558	1.620 185
200	1.618 229	1.605 055	1.610 551
400	1.610 911	1.605 253	1.606 134
800	1.608 106	1.605 293	1.605 446
1600	1.606 742	1.605 303	1.605 341
∞		1.605 32(1)	
		$\langle p_i^4 \rangle$	
100	2137.407	2164.851	2164.780
200	2153.618	2165.594	2165.503
400	2155.764	2165.567	2165.681
800	2161.966	2165.644	2165.613
1600	2162.989	2165.637	2165.622
∞		2165.64(1)	
		$\left\langle P\left(1/r_{ij}^3\right) \right\rangle$	
100	−8.552 39	−7.304 29	−7.554 00
200	−8.123 10	−7.318 37	−7.408 33
400	−7.730 23	−7.324 54	−7.346 32
800	−7.552 88	−7.326 22	−7.333 15
1600	−7.455 34	−7.326 63	−7.328 56
∞		−7.326 8(3)	

TABLE V: Hydrogen molecule, $R = 1.4$ bohr. Convergence of the expectation values computed directly in comparison with those obtained by the integral transform (IT).

K	Direct	IT
	$\langle\delta(\boldsymbol{r}_{iI})\rangle$	
75	0.457 670 262	0.459 447 637
150	0.458 771 435	0.459 653 671
300	0.459 254 845	0.459 666 311
600	0.459 509 138	0.459 667 951
1200	0.459 588 096	0.459 668 101
∞		0.459 668 2(1)
	$\langle\delta(\boldsymbol{r}_{ij})\rangle$	
75	0.016 953 5	0.016 857 29
150	0.016 814 3	0.016 748 22
300	0.016 771 8	0.016 743 95
600	0.016 758 3	0.016 743 32
1200	0.016 761 6	0.016 743 39
∞		0.016 743 4(2)
	$\langle p_i^4\rangle$	
75	13.184 83	13.234 252
150	13.214 49	13.237 555
300	13.227 20	13.237 908
600	13.233 76	13.237 955
1200	13.235 68	13.237 960
∞		13.237 965(5)
	$\left\langle P\left(1/r_{ij}^3\right)\right\rangle$	
75	0.385 92	0.397 508
150	0.392 95	0.397 692
300	0.395 61	0.397 899
600	0.396 59	0.397 956
1200	0.396 34	0.397 944
∞		0.397 95(5)

TABLE VI: Convergence of ρ, see Eq. (32), for the hydrogen molecule at $R = 1.4$ bohr.

K	ρ
75	0.442 126
150	0.443 213
300	0.443 680
600	0.443 925
1200	0.444 001
∞	0.444 04(2)