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# Regularized relativistic corrections for polyelectronic and polyatomic systems with explicitly correlated Gaussians

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## ABSTRACT

Drachmann's regularization approach is implemented for floating explicitly correlated Gaussians (fECGs) and molecular systems. Earlier applications of drachmannized relativistic corrections for molecular systems were hindered due to the unknown analytic matrix elements of  $1/r_{ix}1/r_{jy}$ -type operators with fECGs. In the present work, one of the  $1/r$  factors is approximated by a linear combination of Gaussians, which results in calculable integrals. The numerical approach is found to be precise and robust over a range of molecular systems and nuclear configurations, and thus, it opens the route toward an automated evaluation of high-precision relativistic corrections over potential energy surfaces of polyatomic systems. Furthermore, the newly developed integration approach makes it possible to construct the matrix representation of the square of the electronic Hamiltonian relevant for energy lower-bound as well as time-dependent computations of molecular systems with a flexible and high-precision fECG basis representation.

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The leading-order ( $\alpha^2 E_h$ ) relativistic corrections<sup>1</sup> have been computed to high precision for two-, three, and four-electron atoms<sup>2–8</sup> and two- and three-electron diatomic molecules.<sup>6,9–14</sup> We are aware of a single computation of a polyatomic system ( $H_3^+$ ) for which the regularized leading-order relativistic corrections were computed (at the equilibrium structure).<sup>12</sup>

The terms contributing to the leading-order relativistic correction are large in absolute value and have opposite signs, so the correction values must be converged to several digits to arrive at precise final values. Alternative routes to the mainstream perturbation theory approach have been explored and are promising, potentially also for spectroscopic applications,<sup>11,15–22</sup> but currently available only for two-electron (or two-spin-1/2-fermion<sup>19</sup>) systems.

Hence, it is relevant to pursue also the traditional approach<sup>1</sup> and develop automatization schemes for the precise evaluation of the involved singular operators over generally applicable (explicitly correlated) Gaussian basis sets. Due to the incorrect description of the (electron–electron and electron–nucleus) coalescence points of the non-relativistic wave function represented as a linear combination of explicitly correlated Gaussians (ECGs), the highly localized, short-range operator expectation values must be regularized

to speed up convergence with respect to the basis size.<sup>2,6,12</sup> There have been two major directions to correct for this deficiency of general basis sets: (a) using operator identities, which replace local operators with global expressions, often called “drachmannization,” named after the pioneer of this technique,<sup>2</sup> and (b) using integral transformation techniques,<sup>6,12</sup> which map the short-range behavior to the long-range, for which analytic asymptotic expressions can be derived, and can be used to replace the long-tail part of the integral.

Despite the engaging formal theoretical background<sup>12</sup> of the integral transformation technique,<sup>6</sup> it is critical to be able to identify a lower threshold value for the long-range part, which is to be represented by the analytic asymptotic expression. Numerical experience shows that a considerable amount of manual fiddling is required to find the optimal threshold value (separating the important physical features represented by numerical integration and the asymptotic limiting function).<sup>12,13</sup> This arbitrariness introduces large uncertainties.

For a precise and automated computation of the leading-order relativistic correction value over a multi-dimensional potential energy surface, potentially at hundreds or thousands of nuclear

geometries, a robust methodology is required, which can be used in an automated fashion without much manual adjustment.

The drachmannization approach appears to be more robust than the integral transformation technique since it does not contain any parameters to adjust, but the necessary ECG integrals for molecular systems have been thought to be incalculable (in a closed, analytic form).<sup>23</sup> In particular, molecular computations with clamped nuclei can be efficiently carried out using the so-called floating explicitly correlated Gaussians (fECGs), in which the shifted (“floating”) centers (treated as variational parameters) are necessary to efficiently account for the significant wave function amplitude off-centered from the origin. The  $\langle 1/r_{ix}1/r_{jy} \rangle$ -type integral expressions ( $i, j$  label electron coordinates;  $x, y$  label electron or nuclear coordinates), necessary for the evaluation of the drachmannized relativistic corrections, are not known for fECGs, unless the ECG centers are fixed at the origin (zero shift).

Interestingly, the same type of incalculable integrals appear in lower-bound theory, and most importantly its Pollak–Martinazzo<sup>24,25</sup> version, which has been demonstrated to be powerful for atomic systems (zero-shift ECGs with analytic integrals),<sup>26,27</sup> but no molecular computations have been performed due to the missing integral expressions. Potentially, similar integrals will be required in time-dependent simulations recently proposed with explicitly correlated Gaussians.<sup>28</sup>

In this work, we develop a numerical approach for the computation of the  $\langle 1/r_{ix}1/r_{jy} \rangle$ -type integrals with fECGs by writing one of the  $1/r$  factors as a linear combination of Gaussians. The representation of  $1/r$  as a linear combination of Gaussians has already been successfully used for deformed explicitly correlated Gaussians by Varga and co-workers,<sup>29</sup> using the mathematical scheme of Beylkin and Monzón.<sup>30</sup>

As a result, a robust numerical drachmannization scheme is developed in this work, and regularized relativistic corrections (computable in a black-box fashion) are reported for two-, three-, and four-electron di- and triatomic molecular systems.

As a starting point, the non-relativistic energy and wave function are computed by solving the electronic Schrödinger equation,

$$H\Psi = E\Psi \quad (1)$$

with the Hamiltonian

$$H = -\sum_{i=1}^n \frac{1}{2} \nabla_{r_i}^2 + V \quad (2)$$

including the potential energy

$$V = \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}} - \sum_{i=1}^n \sum_{a=1}^N \frac{Z_a}{|\mathbf{r}_i - \mathbf{R}_a|} + \sum_{a=1}^N \sum_{b>a}^N \frac{Z_a Z_b}{|\mathbf{R}_a - \mathbf{R}_b|}, \quad (3)$$

where the nuclei have charge number  $Z_a$  and are clamped at  $\mathbf{R}_a$  ( $a = 1, \dots, N$ ). The generally applicable and flexible ansatz used to represent the wave function is

$$\Psi = \sum_{\mu=1}^M c_{\mu} \mathcal{A}\{\chi_{\mu} \varphi_{\mu}\}, \quad (4)$$

where  $\mathcal{A}$  is the anti-symmetrization operator (relevant for indistinguishable fermions) and  $\chi$  is the spin function written as a linear

combination of elementary spin functions coupled to the total electronic spin of the system.<sup>31,32</sup> For the spatial part, we use floating explicitly correlated Gaussian functions (fECGs),

$$\varphi_{\mu}(\mathbf{r}, \mathbf{A}_{\mu}, \mathbf{s}_{\mu}) = \exp \left[ -(\mathbf{r} - \mathbf{s}_{\mu})^T (\mathbf{A}_{\mu} \otimes \mathbf{I}_3) (\mathbf{r} - \mathbf{s}_{\mu}) \right], \quad (5)$$

where  $\mathbf{r}$  collects the  $3n$  Cartesian coordinates of the electrons in the system,  $\mathbf{A}_{\mu} \in \mathbb{R}^{n \times n}$  is a positive-definite, symmetric matrix, and  $\mathbf{s}_{\mu} \in \mathbb{R}^{3n}$  will be referred to as the “shift vector.”  $\mathbf{I}_3$  is the three-dimensional unit matrix. The  $\mathbf{A}_{\mu}$  and  $\mathbf{s}_{\mu}$  parameters are optimized by minimization of the non-relativistic energy.

In the non-relativistic quantum electrodynamics approach,<sup>1</sup> the non-relativistic energy is perturbatively corrected by relativistic and QED contributions in terms of increasing orders of the  $\alpha$  fine-structure constant,

$$E = E^{(0)} + \alpha^2 E^{(2)} + \alpha^3 E^{(3)} + \alpha^3 \ln(\alpha) E^{(3,1)} + \dots \quad (6)$$

The  $E^{(2)}$  second-order term, known as the leading-order relativistic correction, can be computed as the expectation value of the Breit–Pauli Hamiltonian,<sup>1</sup>

$$E^{(2)} = \langle \Psi | H_{\text{BP}}^{(2)} | \Psi \rangle, \quad (7)$$

which is written for singlet (or spin averaged) electronic states as

$$H_{\text{BP}}^{(2)} = -\frac{1}{8} \sum_{i=1}^n \nabla_i^2 \nabla_i^2 + \frac{\pi}{2} \sum_{i=1}^n \sum_{a=1}^N Z_a \delta(\mathbf{r}_{ia}) + \pi \sum_{i=1}^n \sum_{j>i}^n \delta(\mathbf{r}_{ij}) + H_{\text{OO}} \quad (8)$$

with

$$H_{\text{OO}} = -\frac{1}{2} \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}} \left( \mathbf{p}_i \mathbf{p}_j + \frac{\mathbf{r}_{ij} (\mathbf{r}_{ij} \mathbf{p}_i) \mathbf{p}_j}{r_{ij}^2} \right). \quad (9)$$

The terms of  $H_{\text{BP}}^{(2)}$  in Eq. (8) have traditional names; they are the mass-velocity term, the one-electron Darwin term, the two-electron Darwin term (combined with the spin–spin Fermi contact interaction), and the orbit–orbit term, respectively. All terms, except the orbit–orbit contribution, include highly localized, singular operators, for which the expectation value with the non-relativistic wave function is inefficiently represented over “smooth” fECG basis functions, i.e., the expectation value converges slowly with respect to the number of basis functions.<sup>12</sup>

The drachmannization technique<sup>2</sup> uses operator identities valid for the exact non-relativistic wave function,  $(T + V)\Psi = E\Psi$  in Eqs. (1) and (2), to replace singular operators with more globally acting operators,

$$\langle \delta(\mathbf{r}_{ij}) \rangle = \frac{1}{4\pi} \left[ 2 \langle \Psi | \frac{1}{r_{ij}} (E - V) | \Psi \rangle - \sum_{k=1}^n \langle \nabla_k \Psi | \frac{1}{r_{ij}} | \nabla_k \Psi \rangle \right], \quad (10)$$

$$\langle \delta(\mathbf{r}_{ia}) \rangle = \frac{1}{2\pi} \left[ 2 \langle \Psi | \frac{1}{r_{ia}} (E - V) | \Psi \rangle - \sum_{k=1}^n \langle \nabla_k \Psi | \frac{1}{r_{ia}} | \nabla_k \Psi \rangle \right], \quad (11)$$

and

$$\left\langle \sum_{i=1}^n \nabla_i^2 \nabla_i^2 \right\rangle = 4 \langle \Psi | (E - V)^2 | \Psi \rangle - 2 \sum_{i=1}^n \sum_{j>i}^n \langle \nabla_i \Psi | \nabla_j^2 \Psi \rangle. \quad (12)$$

During the evaluation of these expectation values, the following integrals appear:

$$\left\langle \frac{1}{r_{ia} r_{kb}} \right\rangle, \quad \left\langle \frac{1}{r_{ij} r_{kb}} \right\rangle, \quad \left\langle \frac{1}{r_{ij} r_{kl}} \right\rangle, \quad (13)$$

for which no analytic result is known with fECG basis functions. In the present work, we propose a numerical approach to compute these integrals to high precision.

We can approximate the  $1/r$  function as a linear combination of Gaussian functions. For practical purposes, this approximation is formulated as

$$\frac{1}{r} \cong \sum_{m=1}^M w_m e^{-p_m r^2}, \quad (14)$$

with the weights and points chosen according to Beylkin and Monzón,<sup>30</sup>

$$w_m = \frac{2}{\sqrt{\pi}} h e^{a+mh} \quad \text{and} \quad p_m = e^{2(a+mh)}, \quad (15)$$

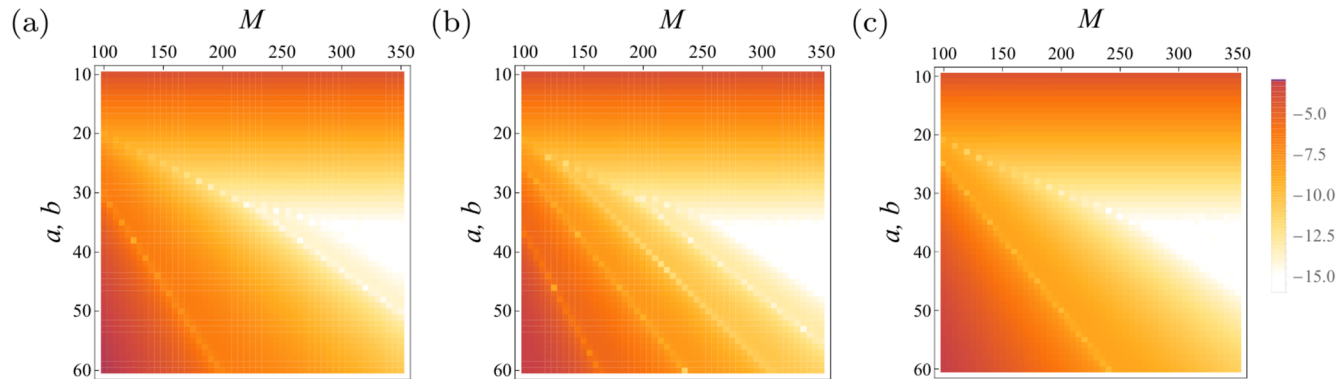
where the step variable is  $h = \frac{b-a}{M}$ . The approximation has three input parameters: the  $M$  number of Gaussian functions and the  $a < 0$  and  $b > 0$  boundary parameters. To better understand the origin of these parameters, we note that the underlying approximation idea starts with considering the following integral:<sup>30,33</sup>

$$r^{-\alpha} = \frac{2}{\Gamma(\alpha/2)} \int_{-\infty}^{\infty} ds e^{-r^2 e^{2s} + \alpha s}, \quad (16)$$

which can be calculated by the  $s = \ln(t/r^2)/2$  substitution. Then, for  $\alpha = 1$ ,

$$\frac{1}{r} = \frac{2}{\sqrt{\pi}} \int_{-\infty}^{\infty} ds e^{-r^2 e^{2s} + s}, \quad (17)$$

and the integral is approximated using the trapezoidal rule. In this numerical approximation, the lower and upper limits are set to some (finite)  $a$  and  $b$  values, respectively. The numerical integration limits  $a$  and  $b$  are chosen so that the value of the integrand is negligible at the boundaries and beyond them. Then, the application of the trapezoidal rule results in Eqs. (14) and (15). The fast convergence of the



**FIG. 1.** Relative error on a logarithmic scale,  $\log|\delta|$ , of the Gaussian approximation, Eqs. (14) and (15) (with  $-a = b$ ), tested for special cases for which analytic expressions are also available: (a)  $U_{kl} = \langle \varphi_k | \frac{1}{r_{lj}} | \varphi_l \rangle$ ; (b)  $U_{kl} = \langle \varphi_k | \frac{1}{r_{lj}} \frac{1}{r_{pq}} | \varphi_l \rangle_{\mathbf{S}=0}$ ; and (c)  $U_{kl} = \langle \varphi_k | \frac{1}{r_{lj}^2} | \varphi_l \rangle$ .  $\delta = [U_{kl}^{(\text{analytic})} - U_{kl}] / U_{kl}$ . Randomly selected pairs of basis functions were used to prepare the figure (deposited in the [supplementary material](#)), and they exemplify the general behavior observed for all basis sets used in this study.

**TABLE I.** Demonstration of the numerical drachmannization approach for the ground state of atoms, He:  $1^1\text{S}$ , Li:  $2^2\text{S}$ , and Be:  $2^1\text{S}$ , and comparison with high-precision reference data from the literature.  $\delta E_{\text{nr}} = E_{\text{ref}} - E_{\text{nr}}$  in  $E_{\text{h}}$ . All computations have been carried out with the same  $(M, a, b) = (200, -31, 31)$  parameterization of the Gaussian expansion, Eqs. (14) and (15). Convergence tables are provided in the [supplementary material](#).

|                   | $-\delta E_{\text{nr}}$ | $-\frac{1}{8} \sum_i \langle \nabla_i^2 \nabla_i^2 \rangle_{\text{rg}}$ | $\sum_{i,a} Z_a \langle \delta(r_{ia}) \rangle_{\text{rg}}$ | $\sum_{i,j} \langle \delta(r_{ij}) \rangle_{\text{rg}}$ |
|-------------------|-------------------------|-------------------------------------------------------------------------|-------------------------------------------------------------|---------------------------------------------------------|
| He                | $6 \times 10^{-11}$     | -13.522 054                                                             | 7.241 717 15                                                | 0.106 345 364                                           |
| He <sup>3</sup>   | $1 \times 10^{-15}$     | -13.522 016 81                                                          | 7.241 717 274                                               | 0.106 345 371 2                                         |
| Li                | $3 \times 10^{-10}$     | -78.557 5                                                               | 41.527 76                                                   | 0.544 322                                               |
| Li <sup>4 a</sup> | $2 \times 10^{-13}$     | -78.556 143 062                                                         | 41.527 828 927                                              | 0.544 329 79                                            |
| Be                | $5 \times 10^{-7}$      | -270.706 5                                                              | 141.475 80                                                  | 1.605 301 5                                             |
| Be <sup>7 a</sup> | $3 \times 10^{-10}$     | -270.703 76                                                             | 141.476 010 4                                               | 1.605 305 33                                            |

<sup>a</sup>More precise non-relativistic energy,  $E_{\text{nr}}$ , is available from Refs. 5 and 35 for Li and Be, respectively, but we could use the regularized relativistic corrections available from the cited work for comparison. The basis sets for the present computations were taken from earlier work.<sup>15,27</sup>

trapezoidal rule, motivating this form of the integrand, was pointed out in Ref. 33.

First, we have tested the Gaussian approximation for three special cases, for which analytic integral expressions are also available. Figure 1 highlights the robustness and excellent performance of the numerical approach. As a result of extensive numerical testing, we conclude that high-precision results can be obtained robustly without manual fiddling of the parameters of Eq. (15). For further computations, we have selected the following set of values:  $M = 200$ ,

$a = -31$ , and  $b = 31$ , which is a computationally well-affordable choice and allows for sufficiently precise results (close to machine precision in double-precision arithmetic) without further adjustment. An alternative, similarly useful and practical parameterization was  $M = 400$ ,  $a = -45$ , and  $b = 45$ , for which the computational cost remains low, and was used to test the  $(M, a, b) = (200, -31, 31)$  parameterization. Further refinement of these parameters is possible in the future, but these choices have already provided excellent results with a low computational cost and thereby open the route

**TABLE II.** Illustration of the enhanced convergence rate by the numerical drachmannization approach developed in this work for the example of the  $H_2$  molecule ( $X^1\Sigma_g^+$ ,  $R_{p-p} = 1.40$  bohr).  $\delta E_{nr} = E_{ref} - E_{nr}$  in  $E_h$ . All computations have been carried out with the same  $(M, a, b) = (200, -31, 31)$  parameterization of the Gaussian expansion, Eqs. (14) and (15). Reference 10:  $E_{nr} = -1.174\,475\,714\,220\,443\,4(5)\,E_h$ .

| $-\delta E_{nr}$           | $-\frac{1}{8}\sum_i\langle\nabla_i^2\nabla_i^2\rangle$ | $\sum_{i,a}Z_a\langle\delta(\mathbf{r}_{ia})\rangle$ | $\sum_{i,j}\langle\delta(\mathbf{r}_{ij})\rangle$ | $\langle H_{BP}^{(2)}\rangle$ |
|----------------------------|--------------------------------------------------------|------------------------------------------------------|---------------------------------------------------|-------------------------------|
| Direct                     |                                                        |                                                      |                                                   |                               |
| $1.7\times 10^{-7}$        | -1.65                                                  | 0.918                                                | 0.0169                                            | -0.205                        |
| $1.6\times 10^{-8}$        | -1.65                                                  | 0.919                                                | 0.0168                                            | -0.205                        |
| $1.4\times 10^{-9}$        | -1.65                                                  | 0.919                                                | 0.016 78                                          | -0.2055                       |
| $3.8\times 10^{-10}$       | -1.654                                                 | 0.919                                                | 0.016 77                                          | -0.2055                       |
| Numerical drachmannization |                                                        |                                                      |                                                   |                               |
| $1.7\times 10^{-7}$        | -1.655                                                 | 0.919 33                                             | 0.016 742                                         | -0.206                        |
| $1.6\times 10^{-8}$        | -1.6548                                                | 0.919 335 5                                          | 0.016 743 1                                       | -0.2058                       |
| $1.4\times 10^{-9}$        | -1.654 80                                              | 0.919 335 7                                          | 0.016 743 21                                      | -0.205 75                     |
| $3.8\times 10^{-10}$       | -1.654 79                                              | 0.919 335 8                                          | 0.016 743 24                                      | -0.205 733                    |
| Reference 10               |                                                        |                                                      |                                                   |                               |
| “Direct”                   | -1.654 837 5(1)                                        | 0.919 37(7)                                          | 0.016 743 5(4)                                    | -0.205 682 (8)                |
| “St. reg.”                 | -1.654 745 (2)                                         | 0.919 336 211 2(18)                                  | 0.016 743 278 1(7)                                | -0.205 689 (2)                |
| “rECG & m.reg.”            | -1.654 744 522 5(1)                                    | 0.919 336 211(2)                                     | 0.016 743 278 3(3)                                | -0.205 688 526(7)             |

**TABLE III.** Molecular systems<sup>a</sup>: numerically drachmannized expectation values and the leading-order relativistic correction.  $-\delta E_{nr}$  is the estimated convergence error, in  $E_h$  of the (variational) non-relativistic energy. All converged and 1–2 additional digits are shown. All computations have been carried out with the same  $(M, a, b) = (200, -31, 31)$  parameterization of the Gaussian expansion. Convergence tables are provided in the [supplementary material](#).

|             | $-\delta E_{nr}$ | $-\frac{1}{8}\sum_i\langle\nabla_i^2\nabla_i^2\rangle_{rg}$ | $\sum_{i,a}Z_a\langle\delta(\mathbf{r}_{ia})\rangle_{rg}$ | $\sum_{i,j}\langle\delta(\mathbf{r}_{ij})\rangle_{rg}$ | $\langle H_{OO}\rangle$ | $\langle H_{BP}^{(2)}\rangle$ |
|-------------|------------------|-------------------------------------------------------------|-----------------------------------------------------------|--------------------------------------------------------|-------------------------|-------------------------------|
| $H_2^+$     | $10^{-12b}$      | -0.624 952 638 6                                            | 0.318 293 258 6                                           | ...                                                    | ...                     | -0.124 978 757 0              |
| $b^{34\ c}$ | $10^{-9}$        | -0.624 952 7                                                | 0.318 293 2                                               | ...                                                    | ...                     | -0.124 978 9                  |
| $H_3^+$     | $10^{-9}$        | -1.933 449 7                                                | 1.089 654 23                                              | 0.018 334 666                                          | -0.057 217 520          | -0.221 442 3                  |
| $i^{12\ c}$ | $10^{-9}$        | -1.933 424                                                  | 1.089 655                                                 | 0.018 335                                              | -0.057 218              | -0.221 422                    |
| $HeH^+$     | $10^{-9}$        | -13.419 497                                                 | 7.216 244 8                                               | 0.101 121 71                                           | -0.141 241 61           | -1.907 804                    |
| $i^{15\ c}$ | $10^{-9}$        | -13.419 29                                                  | 7.216 25                                                  | 0.101 122                                              | -0.141 242              | -1.907 58                     |
| $He_2^+$    | $10^{-8}$        | -23.867 58                                                  | 12.537 54                                                 | 0.117 596 4                                            | -0.086 577              | -3.890 79                     |
| $i^{13\ c}$ | $10^{-8}$        | -23.866 14                                                  | 12.537 51                                                 | 0.117 63                                               | -0.086 58               | -3.889 30                     |
| $H_3$       | $10^{-8}$        | -2.277 870                                                  | 1.236 566                                                 | 0.016 712                                              | -0.046 780 1            | -0.329 754 2                  |
| $He_2$      | $10^{-6}$        | -24.157 271                                                 | 12.660 991                                                | 0.119 967 0                                            | -0.073 154              | -3.965 700                    |

<sup>a</sup>The electronic state and molecular geometry was  $H_2^+$ ,  $\tilde{A}^2\Sigma_u^+$ ;  $R_{p-p} = 12.00$  bohr;  $H_2$ ,  $X^1\Sigma_g^+$ ;  $R_{p-p} = 1.40$  bohr;  $H_3^+$ ,  $1A_1'$ ;  $R_{p-p} = 1.65$  bohr,  $\vartheta_{p_1-p_2-p_3} = 60^\circ$ ;  $H_3$ ,  $1^2\Sigma^+$ ;  $R_{p_1-p_2} = 1.4015$  bohr,  $R_{p_2-p_3} = 5.8113$  bohr,  $\vartheta_{p_1-p_2-p_3} = 180^\circ$ ;  $HeH^+$ ,  $1^1\Sigma^+$ ;  $R_{p-\alpha} = 1.46$  bohr;  $He_2^+$ ,  $1^2\Sigma_u^+$ ;  $R_{\alpha-\alpha} = 2.042$  bohr;  $He_2$ ,  $a(1)^3\Sigma_u^+$ ;  $R_{\alpha-\alpha} = 2.00$  bohr.

<sup>b</sup>The non-relativistic energy has been reported with higher precision in Ref. 36.

<sup>c</sup>Earlier available computation with regularization type: integral transform (i)<sup>6,12</sup>, special basis set (b).<sup>34</sup>

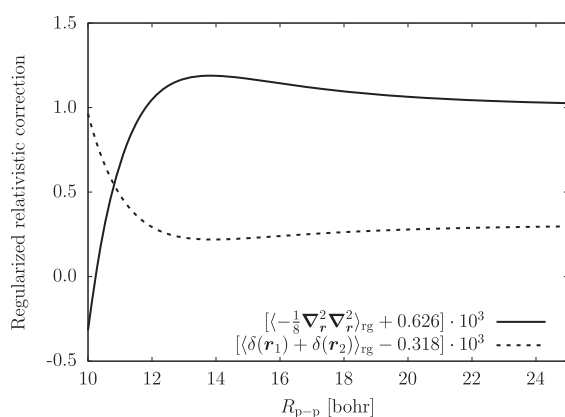
for the computation of relativistic corrections for polyelectronic and polyatomic molecular systems with unprecedented precision in an automated manner.

Tables I and II present the test results of this numerical drachmannization approach for two-, three-, and four-electron atoms and the two-electron hydrogen molecule, for which benchmark-quality data were already available in the literature. In these examples, we computed the ground state for each system, but the approach is similarly applicable to excited states, too.

New numerical results for two-, three-, and four-electron di- and triatomic molecular systems are reported in Table III. These results are the first computation of these leading-order relativistic corrections or improve upon the already available values in the literature. Furthermore, we report the curve of relativistic corrections to the  $\text{H}_2^+ \tilde{A}^2\Sigma_u^+$  electronic state (Fig. 2) to demonstrate the general applicability of the numerical drachmannization approach along potential energy curves.

This work reports a robust and generally applicable numerical drachmannization approach for the computation of the leading-order relativistic corrections with floating explicitly correlated Gaussian basis functions. Formerly incalculable  $\langle 1/r_{ix}1/r_{jy} \rangle$ -type floating ECG integrals are made calculable using a simple and robust Gaussian approximation to one of the  $1/r$  factors. The computational approach is demonstrated to be numerically robust and generally applicable for two-, three-, and four-electron atomic, diatomic, and polyatomic systems and along potential energy curves (and potentially, surfaces). The numerical drachmannization approach developed in this work opens the route to the automated computation of high-precision relativistic corrections to potential energy curves and surfaces in the future.

The supplementary material includes (1) details of the integral calculation and implementation; (2) convergence tables; and (3) basis set parameterizations.



**FIG. 2.** Regularized relativistic corrections to the  $\text{H}_2^+ \tilde{A}^2\Sigma_u^+$  electronic state near the local minimum (near  $R_{pp} = 12.5$  bohr) computed by the automated numerical drachmannization approach proposed in this work. The computed values confirm (and are more precise) than the ones reported by Kennedy and Howells using special basis functions.<sup>34</sup>

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## AUTHOR DECLARATIONS

### Conflict of Interest

The authors have no conflicts to disclose.

### Author Contributions

**Balázs Rácsai:** Investigation (equal); Methodology (equal); Software (equal); Writing – original draft (equal); Writing – review & editing (equal). **Dávid Ferenc:** Investigation (equal); Methodology (equal); Software (equal); Writing – original draft (equal); Writing – review & editing (equal). **Ádám Margócsy:** Investigation (equal); Methodology (equal); Software (equal); Writing – original draft (equal); Writing – review & editing (equal). **Edit Mátyus:** Investigation (equal); Methodology (equal); Software (equal); Writing – original draft (equal); Writing – review & editing (equal).

## DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#).

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