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# Explicitly correlated Gaussian functions in variational calculations: The ground state of the beryllium atom

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Explicitly correlated Gaussian functions are applied to extensive variational calculations of the $^1S$ ground state of the beryllium atom. The convergence of the energy with respect to the basis-set expansion length is investigated. The nonrelativistic clamped-nuclei energy computed from a 1200-term wave function equals $-14.667\,355$ hartree and is in error by about 1 cm$^{-1}$. This is the lowest variational upper bound to the beryllium ground-state energy reported to date and it shows that recent empirical estimates of the nonrelativistic energy of the Be atom lie slightly too high. Several expectation values, including powers of interparticle distances and the Dirac $\delta$ function, are computed. The nuclear magnetic shielding constant, the magnetic susceptibility, the specific mass shifts, the transition isotope shift, and the electron density at the nucleus position are evaluated.

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## I. INTRODUCTION

Thirty-five years ago Boys [1] and Singer [2] proposed to represent a many-electron wave function in the form $\Psi=\Sigma_k c_k \exp(-Q_k)$, where $Q_k$ is a positive definite quadratic form in interparticle distances. We refer to this type of function as exponentially correlated Gaussian functions (ECG). This type of function, in connection with a suitable optimization procedure, and thanks to the progress in computer techniques, provides a very promising computational tool. The method has already proven extremely good on two-electron systems. The case of the helium atom obtaining microhartree accuracy does not present any difficulties [3–5]. Already in the 1980's Gaussian-type-geminal functions, the two electron case of the ECG, allowed for an accuracy of a few cm$^{-1}$ when applied to the hydrogen molecule [6–8]. During the last decade, the energy error was decreased to a fraction of cm$^{-1}$ [4,9,10] to reach finally the level of accuracy that has never been obtained before for any molecular system [11]. A possibility of obtaining results of the same quality for HeH$^+$ and H$_3{}^+$ has also been presented [4,10,12]. Application of the ECG to three-electron systems also results in high accuracy as has been shown for Li [13] and H$_3$ [10,14]. A very good agreement with experimental spectroscopic data has been presented for helium dimer cation, He$_2{}^+$ [15]. Encouraging results have also been obtained in the case of the four-electron LiH molecule [14]. In this work, we employed the ECG to challenge another four-electron system: beryllium atom in its ground $^1S$ state.

The most accurate experimental total energy of the ground state of beryllium atom E$_{tot}$ is obtained by adding together the first and second ionization energies measured by Holmström and Johansson [16] and the theoretical value of the total energy for Be$^{2+}$. The latter component, corresponding to a sum of the third and fourth ionization energies, is known more accurately from the theoretical calculations of Drake [17] than from the experiment. The total energy obtained this way [18] is $-14.669\,332\,4$ hartree ($E_H$).

From the computational point of view, the total energy consists of several contributions. The major one, usually referred to as the nonrelativistic energy, $E_{\rm nr}$, involves the Coulomb interactions and the kinetic energy of the electrons. It is often calculated as a sum of Hartree-Fock, $E_{\rm HF}$, and correlation, $E_{\rm corr}$, energies. All the other contributions to the total energy of Be amount to ca. $-2\times10^{-3}E_H$, where $E_H=1$ hartree, which is a relatively small fraction of $E_{tot}$, but it must not be neglected when high accuracy is expected. Several non-Coulomb factors account for the contributions. Among them, the finite mass of the nucleus, and the relativistic and radiative effects, are the leading ones. Extensive work has been done towards determining the values of these corrections [18–20]. Bunge's configuration interaction (CI) calculations [19] give $E_{tot}-E_{\rm nr}=-2047(30)\times10^{-6}E_H$, the same quantity calculated from the data given in the review by Mårtensson-Pendrill *et al.* [20] amounts to $-1956(25)\times10^{-6}E_H$. Most recently the sum of the corrections has been estimated by Lindroth *et al.* [18] as being $-1979(2)\times10^{-6}E_H$. Subtracting this value from the experimental total energy $E_{tot}$ leads to an estimate for the "experimental" nonrelativistic energy [18]

$$E_{\rm nr}=-14.667\,353(2)E_H\,. \quad (1)$$

This number could serve as a reference to the energy of the ground state of Be.

While the main corrections are known to within a few microhartrees, the theoretically determined nonrelativistic energy still gives a major contribution to the uncertainty of $E_{tot}$. An extensive review of various computational approximations and a discussion of the corrections needed to perform a comparison between theory and experiment can be found in Ref. [20]. Its authors, because of the apparent discrepancy between the theory and the experiment, try to examine possible sources of this discrepancy, among them are the nonrelativistic energy and the mass polarization energy.

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Highly accurate values of these quantities will be reported in the present paper, helping to resolve the problem and responding to their call that "more precise calculations of both relativistic and nonrelativistic few-electron systems are needed." Most of the nonrelativistic energy estimates come from perturbational computations or some extrapolation procedures with poorly determined or undetermined error bars. On the other hand, the best variational calculations, which give strict upper bound to $E_{\mathrm{nr}}$, appear to be as much as hundreds of microhartrees in error. Therefore, as Lindroth *et al.* concluded [18], "An accurate calculation of a nonrelativistic energy for Be thus remains a challenge to be pursued."

The purpose of this work is to establish a more accurate reference for the energy and several expectation values. We are going to show that the ECG yield energies 1–2 orders of magnitude more accurate than any other variational wave functions and allow us to narrow the uncertainty in the value of $E_{\mathrm{nr}}$. This, in turn, will enable more detailed analysis of all the corrections.

The nonrelativistic Hamiltonian and the ECG functions are defined in Sec. II, together with a short description of the optimization strategy. This is the choice of the explicitly correlated wave functions and the effectiveness of the optimization algorithm, which enable obtaining an accurate energy with basis-set size several times smaller than those used in previous variational calculations. Section III presents results concerning the ground-state energy as well as several expectation values. In 1988 Wen *et al.* [21] reported measurements of isotope shifts in the spectrum of beryllium. They remarked that "Accurate *ab initio* calculation of this quantity poses a challenge to theory which, to our knowledge, has not yet been met." In Sec. III C, we derive the theoretical isotope shift and compare it directly with the experimental one. Finally, Sec. IV contains the conclusions.

## II. METHOD

The nonrelativistic Hamiltonian employed in this calculation, when expressed in atomic units, has the form

$$\hat{H}=-\frac{1}{2}\sum_{i=1}^{4}\nabla_i^2+\sum_{i=1}^{3}\sum_{j=i+1}^{4}\frac{1}{r_{ij}}-4\sum_{i=1}^{4}\frac{1}{r_i}. \tag{2}$$

It does not include mass polarization contribution, and corresponds to an infinite-mass nucleus. Our trial wave function can be written in the form of an antisymmetrized linear combination

$$\Psi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4)=\hat{\mathscr{A}}\left(\Theta_{S,M_S}\sum_{k=1}^{K}c_k\psi_k\right), \tag{3}$$

where $K$ is the number of basis functions, $c_k$ are variationally determined expansion coefficients, and $\hat{\mathscr{A}}$ represents the four-particle antisymmetrizer

$$\hat{\mathscr{A}}=\sum_{l=1}^{4!}\epsilon_{\mathscr{P}_l}\mathscr{P}_l, \tag{4}$$

where $\epsilon_{\mathscr{P}_l}=\pm 1$, depending on the parity of the electron coordinate permutation, $\mathscr{P}_l$. $\Theta_{S,M_S}$ is a four-electron spin eigenfunction fulfilling two eigenequations simultaneously

$$\hat{S}^2\,\Theta_{S,M_S}=S(S+1)\,\Theta_{S,M_S} \tag{5}$$

and

$$\hat{S}_z\,\Theta_{S,M_S}=M_S\,\Theta_{S,M_S}. \tag{6}$$

For the singlet state of a four-electron system, there are two orthogonal spin functions, both corresponding to $S=M_S=0$, e.g.,

$$\Theta_{0,0}^{(1)}=\frac{1}{2}[\alpha\beta\alpha\beta-\beta\alpha\alpha\beta-\alpha\beta\beta\alpha+\beta\alpha\beta\alpha] \tag{7}$$

and

$$\Theta_{0,0}^{(2)}=\frac{1}{2\sqrt{3}}[-\beta\alpha\beta\alpha-\alpha\beta\beta\alpha+2\beta\beta\alpha\alpha+2\alpha\alpha\beta\beta-\alpha\beta\alpha\beta-\beta\alpha\alpha\beta]. \tag{8}$$

It has been proven [14] that only one such function is needed to ensure convergence of eigenvalues to the exact root of the Hamiltonian. The former one has been adopted in these computations. The spatial part of the basis function is of the form

$$\psi_k(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4)=\exp\left[-\sum_{i=1}^{4}\sum_{j=i+1}^{5}a_{ij,k}r_{ij}^2\right], \tag{9}$$

where $i$, $j$ label all the five particles: four electrons and the $\mathrm{Be}^{4+}$ nucleus. $a_{ij,k}$ denote nonlinear variational parameters—ten per each basis function.

### Optimization of the wave function

Obviously, the variational energy of the system

$$E(\{c_k\},\{a_{ij,k}\})=\frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}, \tag{10}$$

depends on the set of linear and nonlinear parameters of the trial function, $\Psi$. To find the global minimum of the functional (10) with respect to all these parameters is practically an impossible task and no universal algorithm solving this problem exists. For instance, with the 1000-term wave function of the ansatz (3), energy becomes a function of 10 000 nonlinear parameters, and it is not feasible to perform the full optimization of such a function and find the global minimum. On the other hand, as experience shows, proper optimization of these nonlinear parameters is crucial to obtaining highly accurate results. Several ways of solving this problem have been proposed. Thakkar and Smith [22] developed the random tempering method allowing us to reduce the number of the optimized parameters. To find the minimum, Kozłowski and Adamowicz employed analytical first derivatives of the variational energy with respect to the nonlinear parameters [23]. A simple method of sampling has also been used with some success [24].

TABLE I. The energy convergence with the wave function expansion increase. $E_K$ is the energy obtained from the $K$-term wave function, $\Delta E_K = E_{K/2} - E_K$. $L(0.01)$ is the convergence factor described in Sec. III A and $-\langle V\rangle/2\langle T\rangle$ is the virial coefficient.

| $K$ | $E_K/E_H$ | $\Delta E_K$ (cm$^{-1}$) | $\frac{\Delta E_{K/2}}{\Delta E_K}$ | $L(0.01)$ | $-\frac{\langle V\rangle}{2\langle T\rangle}$ |
|---|---|---|---|---|---|
| 50 | −14.665 053 934 4 | | | | 0.999 998 195 9 |
| 75 | −14.666 444 767 0 | | | | 1.000 002 669 1 |
| 100 | −14.666 892 195 7 | 403.457 | | | 1.000 002 168 5 |
| 150 | −14.667 185 772 5 | 162.634 | | | 0.999 996 215 3 |
| 200 | −14.667 271 964 6 | 83.351 | 4.84 | 370 | 0.999 998 386 7 |
| 300 | −14.667 317 471 6 | 28.905 | 5.63 | 410 | 0.999 999 264 0 |
| 400 | −14.667 335 166 9 | 13.872 | 6.01 | 397 | 0.999 999 764 4 |
| 600 | −14.667 350 194 8 | 7.182 | 4.02 | 118 | 0.999 999 865 4 |
| 800 | −14.667 353 426 7 | 4.008 | 3.46 | 75 | 0.999 999 972 5 |
| 1200 | −14.667 355 021 7 | 1.059 | 6.78 | 35 | 0.999 999 973 4 |

In this work we used some limited form of the optimization leading to local minima with sufficiently low energy. In one step we optimize simultaneously only ten nonlinear parameters in a given term $\psi_k$ of the $K$-term wave function using Powell's conjugate direction method [25]. A cycle consisting of $K$ such steps is then repeated as many times as needed to fulfill an imposed criterion. The domain for the parameters search has been limited by the square-integrability condition and negative values of the individual $a_{ij,k}$ parameters were allowed. During such an optimization, only one row and one column of the Hamiltonian and overlap matrices need to be updated as the nonlinear parameters of the selected term change. Without the savings resulting from this observation, the computations are simply not feasible. One has to emphasize that the set of the parameters found in each step is optimal only with respect to the fixed set of the other parameters and one cycle alone is not able to give the required accuracy. Only repeating one cycle after another makes these parameters converge to a minimum. Of course, in practice one has to compromise between the number of reoptimizing cycles and the cost of this calculation.

## III. RESULTS AND DISCUSSION

### A. The ground-state energy

The computations were carried out for several expansion lengths, ranging from $K=50$ to $K=1200$ basis functions. The energies obtained are listed in Table I. The first conclusion that can be drawn from the table is a significant improvement in energy over any variational calculations reported to date. Already the 150-term wave function yields better energy than the lowest previous result of Fisher [26]. Energies obtained from the longest expansions give errors at least one order of magnitude smaller than any other variational results. The best previous variational calculations come from Sims and Hagström [27], Bunge [19], Clementi *et al.* [28], and most recently from Chung *et al.* [29] and Fisher [26] (see Table II). The reported upper bounds to the nonrelativistic ground-state energy of Be are, respectively, 177 cm$^{-1}$, 99 cm$^{-1}$, 86 cm$^{-1}$, 68 cm$^{-1}$, and 53 cm$^{-1}$ above the "experimental" energy (1) published by Lindroth *et al.* Our 1200-term wave function gives energy even lower than this reference.

Apart from the variational computations, many perturbational results have been presented. Correlation energies, calculated directly from a perturbation method or as a difference $E - E_{\mathrm{HF}}$, where $E=\min\{E_{\mathrm{UB}}, E_{\mathrm{estim}}\}$, are displayed in Table II. $E_{\mathrm{UB}}$, listed in the first column of the table, is an energy computed directly from variational calculations, and represents a strict upper bound to the exact nonrelativistic energy. $E_{\mathrm{estim}}$ is estimated either from perturbational computations or from extrapolation to an infinite basis set. Broad discussion of difficulties in obtaining microhartree accuracy for $E_{\mathrm{corr}}$ can be found in Ref. [20]. The most accurate estimates of the correlation energy are close to $-94.3\times 10^{-3}E_H$, e.g., $-94.29\times 10^{-3}E_H$ computed by Alexander *et al.* [4], $-94.35\times 10^{-3}E_H$ by Olsen and Sundholm [30], $-94.34\times 10^{-3}E_H$ by Davidson *et al.* [31] or, most recently, $-94.249\times 10^{-3}E_H$ by Noga *et al.* [32]. For comparison, our 1200-term wave function yields $E_{\mathrm{corr}} = -94.332\times 10^{-3}E_H$.

The expansion lengths, $K$, listed in the first column of Table I, comprise two geometrical series: $K=50$, 100, 200, 400, and 800, and $K=75$, 150, 300, 600, and 1200. Except for $K=50$ and $K=75$, for each $E_K$—the energy obtained from the wave function of the size $K$—we can determine $E_{K/2}$ and calculate the difference $\Delta E_K = E_{K/2} - E_K$. The effect of the basis-set doubling with increasing $K$ allows one to assess the convergence rate without referring to any external value of the energy. This is particularly important when no exact reference energy exists. As can be seen from the third and fourth columns of the table, where values of $\Delta E_K$ and $\Delta E_{K/2}/\Delta E_K$ are displayed, each doubling of $K$ gives energy lowering three or more times smaller than that of $K/2$. Assuming that this tendency is preserved for still longer expansions, and that the function (3) is complete in pertinent Hilbert space, we can estimate the true eigenvalue of the Hamiltonian (2). The extrapolation leads to the conclusion that our upper bound computed from the 1200-term wave function lies about 1 cm$^{-1}$ above the exact lowest eigenvalue of the Hamiltonian. Our estimate for the nonrelativistic ground-state energy of Be is

$$E_{\mathrm{nr}} = -14.667\,360(2)E_H \tag{11}$$

and the correlation energy corresponding to the new value is

TABLE II. Comparison of nonrelativistic energies and correlation energies obtained with various theoretical methods.

| $E_{\mathrm{UB}}$[a]$/E_H$ | $E_{\mathrm{estim}}$[b]$/E_H$ | $10^3E_{\mathrm{corr}}$[c]$/E_H$ | Ref. |
|---|---|---|---|
| −14.6577 | | −84.7 | Gentner and Burke [37], 25-term Hylleraas wave function |
| −14.666 547 | | −93.524 | Sims and Hagström [27], 107-term Hylleraas CI wave function |
| −14.665 870 | | −92.847 | Fisher and Saxena [38], MCHF, 52 configurations |
| −14.665 87 | | −92.85 | Clary and Handy [39], 40-term Hylleraas CI wave function |
| −14.666 32 | | −93.30 | Sims and Hagström [40], 57-term Hylleraas CI wave function |
| −14.666 902 | −14.667 328 | −94.305 | Bunge [19], 650-term CI wave function |
| | −14.665 96 | −92.260 | Lindgren and Salomonson [41], coupled cluster method |
| | | −94.29 | Alexander *et al.* [42], estimated |
| | −14.660 613 | −87.768 | Urban *et al.* [43], coupled cluster method |
| | −14.666 69 | −93.667 | Salomonson and Öster [44], coupled cluster method |
| −14.665 570 | −14.667 37 | −94.35 | Olsen and Sundholm [30], MCHF |
| −14.666 960 | | −93.9 | Clementi *et al.* [28], CI wave function |
| | −14.667 36 | −94.34 | Davidson *et al.* [31], estimated |
| | −14.671 05 | −95.15 | Liu and Kelly [45], coupled cluster method |
| −14.662 834 | | −89.811 | Schwegler, Kozłowski, and Adamowicz [36], 150-term ECG |
| −14.667 043 | −14.667 349 | −94.326 | Chung *et al.* [29], CI wave function |
| −14.667 113 | −14.667 315 | −94.292 | Fisher [26], MCHF, 3381 configurations |
| −14.666 89 | | −93.87 | Weiss *et al.* [46], CI wave function |
| | −14.667 261 | −94.249 | Noga *et al.* [32], R12-coupled cluster method |
| −14.667 355 | −14.667 360 | −94.337 | This work, 1200-term ECG |
| | −14.667 353(2) | −94.330 | Lindroth *et al.* [18], "experimental" nonrelativistic |

[a] $E_{\mathrm{UB}}$—energies computed directly from variational calculations, representing a strict upper bound to the exact eigenvalues.

[b] $E_{\mathrm{estim}}$—energies estimated either from perturbational computations or from extrapolation to an infinite basis set.

[c] $E_{\mathrm{corr}}$—correlation energies computed by means of a perturbation method or calculated as a difference $E-E_{\mathrm{HF}}$, where $E_{\mathrm{HF}}=-14.573\,023E_H$ [20,31,47] and $E=\min\{E_{\mathrm{UB}},E_{\mathrm{estim}}\}$.

$-94.337\times10^{-3}E_H$. In light of these results, the "experimental" energy by Lindroth *et al.* (1) seems to lie slightly too high.

As mentioned in the previous section the optimization procedure has a limiting threshold imposed. The procedure performs as many cycles as is needed to obtain the energy lowering smaller than $0.01\times10^{-6}E_H$ per cycle. The fifth column of Table I contains a cycle number, $L(0.01)$, at which this condition has been fulfilled. As we can see, longer expansions ensure faster convergence. The 1200-term wave function needs only 35 cycles to converge below this threshold, whereas for the 50–150-term wave functions, we never managed to gain such convergence and stopped after 500 cycles.

The convergence of the energy with growing $K$ is relatively fast and compares favorably with any CI calculations. Nowadays dealing with dense matrices of order 1000 is a routine and not a very costly task. The calculations presented here have been performed on regular workstations. Two completely different and independent programs have been used in these calculations. Each program implements different integral formulas in the matrix elements routines. Also several independent diagonalization routines have been applied to check the computational process. The energies obtained from these two sources, and additionally computed in both 16- and 32-digit precision, differ at most on the 14th significant figure.

An atomic wave function can be additionally optimized through a scaling procedure. Such a new scaled wave function

$$\Psi_\eta=\eta^6\Psi(\eta\vec{r}_1,\eta\vec{r}_2,\eta\vec{r}_3,\eta\vec{r}_4) \tag{12}$$

would yield still lower energy if the scale factor $\eta$ is chosen properly. The optimum $\eta$ can be determined from the virial theorem, which gives

$$\eta=-\frac{\langle\hat{V}\rangle}{2\langle\hat{T}\rangle}, \tag{13}$$

where $\langle\hat{V}\rangle$ and $\langle\hat{T}\rangle$ are the expectation values of the potential and kinetic energy operators, respectively. The exact wave function describing a stable state of an atom has $\eta=1$. The scale factors computed from Eq. (13) for each $K$ are displayed in the last column of Table I. The multidimensional optimization of the ECG wave function is not uniform in all $r$ coordinates, hence, the virial theorem does not have to be satisfied automatically. It turned out, however, that after ex-

TABLE III. The expectation values of the ground-state beryllium atom. $r_{ee}$ and $r_{en}$ are the electron-electron and electron-nucleus distance operators, respectively, $\delta(r)$ is the Dirac $\delta$ operator. All the expectation values are in atomic units. A digit in parentheses following each $K=\infty$ entry is an estimated deviation on the last decimal figure.

| $K$ | $\langle r_{ee}^{-2}\rangle$ | $\langle r_{en}^{-2}\rangle$ | $\langle r_{ee}^{-1}\rangle$ | $\langle r_{en}^{-1}\rangle$ | $\langle r_{ee}\rangle$ | $\langle r_{en}\rangle$ |
|---|---|---|---|---|---|---|
| 50 | 1.595 075 | 14.387 61 | 0.729 575 1 | 2.106 725 7 | 2.539 034 | 1.490 370 |
| 75 | 1.590 633 | 14.391 40 | 0.729 283 0 | 2.106 781 8 | 2.541 794 | 1.491 569 |
| 100 | 1.590 231 | 14.395 14 | 0.729 217 9 | 2.106 814 3 | 2.543 191 | 1.492 151 |
| 150 | 1.589 914 | 14.398 12 | 0.729 169 0 | 2.106 843 5 | 2.544 334 | 1.492 662 |
| 200 | 1.589 745 | 14.398 66 | 0.729 145 1 | 2.106 841 4 | 2.544 779 | 1.492 870 |
| 300 | 1.589 566 | 14.398 79 | 0.729 132 3 | 2.106 840 7 | 2.544 956 | 1.492 945 |
| 400 | 1.589 531 | 14.398 92 | 0.729 124 9 | 2.106 839 2 | 2.545 100 | 1.493 009 |
| 600 | 1.589 505 | 14.399 30 | 0.729 118 3 | 2.106 838 4 | 2.545 234 | 1.493 076 |
| 800 | 1.589 495 | 14.399 36 | 0.729 116 5 | 2.106 837 9 | 2.545 269 | 1.493 092 |
| 1200 | 1.589 487 | 14.399 39 | 0.729 115 9 | 2.106 837 9 | 2.545 279 | 1.493 097 |
| $\infty$ | 1.589 458(7) | 14.399 52(4) | 0.729 112 1(9) | 2.106 837 4(5) | 2.545 35(2) | 1.493 14(2) |

| $K$ | $\langle r_{ee}^{2}\rangle$ | $\langle r_{en}^{2}\rangle$ | $\langle r_{ee}^{3}\rangle$ | $\langle r_{en}^{3}\rangle$ | $\langle r_{ee}^{4}\rangle$ | $\langle r_{en}^{4}\rangle$ |
|---|---|---|---|---|---|---|
| 50 | 8.743 38 | 4.030 42 | 36.5323 | 13.9228 | 177.371 | 55.875 |
| 75 | 8.770 56 | 4.044 13 | 36.7420 | 14.0368 | 178.875 | 56.736 |
| 100 | 8.785 23 | 4.050 59 | 36.8681 | 14.0911 | 179.946 | 57.168 |
| 150 | 8.797 66 | 4.056 47 | 36.9760 | 14.1427 | 180.838 | 57.593 |
| 200 | 8.802 68 | 4.058 92 | 37.0222 | 14.1653 | 181.249 | 57.792 |
| 300 | 8.804 62 | 4.059 80 | 37.0393 | 14.1734 | 181.392 | 57.862 |
| 400 | 8.806 12 | 4.060 47 | 37.0520 | 14.1791 | 181.495 | 57.910 |
| 600 | 8.807 65 | 4.061 24 | 37.0669 | 14.1865 | 181.640 | 57.982 |
| 800 | 8.808 04 | 4.061 41 | 37.0705 | 14.1882 | 181.672 | 57.997 |
| 1200 | 8.808 16 | 4.061 48 | 37.0718 | 14.1888 | 181.685 | 58.003 |
| $\infty$ | 8.809 0(3) | 4.061 9(2) | 37.081(4) | 14.193(2) | 181.79(5) | 58.05(3) |

| $K$ | $\langle\delta(r_{ee})\rangle$ | $\langle\delta(r_{en})\rangle$ | $-\langle\nabla_i\nabla_j\rangle$ | Kinetic energy |
|---|---|---|---|---|
| 50 | 0.279 76 | 8.6219 | 0.465 272 | 14.665 106 848 |
| 75 | 0.272 44 | 8.6441 | 0.462 297 | 14.666 366 475 |
| 100 | 0.271 29 | 8.7054 | 0.461 263 | 14.666 828 585 |
| 150 | 0.270 39 | 8.7753 | 0.460 701 | 14.667 296 795 |
| 200 | 0.269 70 | 8.7846 | 0.460 468 | 14.667 319 289 |
| 300 | 0.268 80 | 8.7935 | 0.460 351 | 14.667 339 061 |
| 400 | 0.268 49 | 8.7938 | 0.460 286 | 14.667 342 077 |
| 600 | 0.268 19 | 8.8170 | 0.460 247 | 14.667 354 144 |
| 800 | 0.268 04 | 8.8229 | 0.460 234 | 14.667 354 234 |
| 1200 | 0.267 84 | 8.8279 | 0.460 229 | 14.667 355 803 |
| $\infty$ | 0.266 9(6) | 8.86(2) | 0.460 205(3) | 14.667 360(2) |

tensive optimization the wave functions have the scaling factors so close to one that the scaling brings practically no further energy lowering.

### B. The expectation values

The wave functions obtained as described in previous sections have been subsequently employed in determination of expectation values of several simple operators:

$$\langle\hat{o}\rangle=\frac{\langle\Psi|\hat{o}|\Psi\rangle}{\langle\Psi|\Psi\rangle}. \tag{14}$$

The expectation value of the operator representing the inverse electron-nucleus distance $r_{en}^{-1}$ has the fastest convergence of all the expectation values listed in Table III. Only the eighth significant figure appears to be uncertain. Five decimal digits seem to be stable for the expectation value of the inverse interelectron distance operator, $r_{ee}^{-1}$. Both the operators are the components of the Hamiltonian, which explains the best convergence of their expectation values. The other moments, $\langle r_{en}^{n}\rangle$ and $\langle r_{ee}^{n}\rangle$, with $n=-2$, 1, 2, 3, and 4, converge slower but still, for the values computed from 1200-term wave function, at least four significant figures can be accepted. The uncertainty grows when $n$ increases. The higher the power of $r$, the more distant regions of the electron density distribution are sampled, hence, the more sensitive to the quality of the wave function is the expectation value. The $\langle r_{en}^{n}\rangle$ values are also known from Esquivel and Bunge's calculations [33] who employed a 650-term CI wave function [19]. Their density moments differ by no more than 0.5% from those listed in Table III for $K=1200$.

The Dirac $\delta$-function operators, $\delta(r_{en})$ and $\delta(r_{ee})$ exhibit the poorest convergence of their expectation values. It is well known that Gaussian-functions have unphysical asymptotic behavior. It concerns not only distant regions of the electron density distribution, affecting higher moments of $r$, but also the closest surrounding of the nucleus which, in turn, is important for obtaining accurate energy. An exact wave function should obey pertinent cusp conditions. The Gaussian-type functions can never fulfill such conditions despite using infinitely long expansion. The relatively slow convergence of $\langle\delta(r_{en})\rangle$ and $\langle\delta(r_{ee})\rangle$ is another evidence of this feature. Nevertheless, the poorly represented region of space around the nucleus can be arbitrarily minimized in the process of the optimization as has been shown in case of the energy. The expectation values of $\delta(r_{en})$ and $\delta(r_{ee})$ are the components of the relativistic Hamiltonian responsible for penetration effects. $\langle\delta(r_{en})\rangle$ gives also raise to the electron density at the nucleus, $\rho(0)=16\pi\langle\delta(r_{en})\rangle$. The value calculated from the extrapolated expectation value is

$$\rho(0)=445(1)\ \text{bohr}^{-1}. \tag{15}$$

This value can be compared with 444.472 $\text{bohr}^{-1}$ of Bunge [34] and 444.466 $\text{bohr}^{-1}$ of Esquivel and Bunge [33]. It is worth noting that all the expectation values reported in Table III converge monotonically. This important feature enables application of a similar extrapolation procedure that has been used in the case of the energy as described in Sec. III A. The expectation values extrapolated for $K\rightarrow\infty$ can be found in Table III with each entry followed by an estimated error bar.

### C. The finite nuclear mass correction

The effect of the finite mass of the nucleus can be treated as a perturbation in $m_r/M$, where $M$ is the nuclear mass and $m_r=m_eM/m_e+M$ is the reduced electron mass. Because $^9$Be, the only stable nuclide of beryllium, is over 16 000 times heavier than the electron, it is sufficient to consider only the first-order terms in the perturbation series. In this case, the normal mass shift (NMS), the major part of the nuclear mass correction, can be obtained simply by rescaling the total energy. The normal mass shift is the same for all the energy levels. The specific mass shift (SMS) is much smaller than NMS and changes from state to state. It has its origin in the mass polarization term, $-m_r/M\Sigma_i\Sigma_{j>i}\nabla_i\nabla_j$, of the finite mass Hamiltonian. The SMS, as a first-order correction to the energy, has the form

$$\Delta E_{SMS}=-\frac{m_r}{M}\left\langle\Psi\left|\sum_{i=1}^{3}\sum_{j=i+1}^{4}\nabla_i\cdot\nabla_j\right|\Psi\right\rangle, \tag{16}$$

where $\Psi$ is the eigenfunction of the clamped nucleus Hamiltonian. For beryllium, the specific mass shift parameter, $S=-\langle\nabla_i\nabla_j\rangle$, has been estimated by Fisher [26] using the multiconfiguration Hartree-Fock (MCHF) method as equal to 0.460 69 a.u. Chung *et al.* [29] obtained $S=0.4618$ a.u. applying CI wave function. This expectation value depends strongly on how much of the electron correlation is taken into account, therefore, it comprises another sensitive check on the quality of the wave function. As can be seen from Table III, $\langle\nabla_i\nabla_j\rangle$ converges quite fast and five significant figures can be recognized as stable. The 1200-term wave function yields $S=0.460\,229$ a.u., the extrapolated value is

$$S=0.460\,205(3)\ \text{a.u.} \tag{17}$$

and the SMS derived from (17) for $^9$Be and for $^{10}$Be, the unstable but long-lived nuclide, are

$$\Delta E_{SMS}^{^9Be}=28.0182(2)\times10^{-6}E_H \tag{18}$$

and

$$\Delta E_{SMS}^{^{10}Be}=25.2159(2)\times10^{-6}E_H. \tag{19}$$

Obviously, the isotope substitution affects the ionization energy, resulting in the transition isotope shift (TIS), the quantity which can be obtained also experimentally. The replacement of $^9$Be by $^{10}$Be in the neutral atom and in the beryllium cation, Be$^+$, gives

$$\Delta E_{TIS}=(\Delta E_{SMS}^{^{10}Be^+}-\Delta E_{SMS}^{^{10}Be})-(\Delta E_{SMS}^{^9Be^+}-\Delta E_{SMS}^{^9Be}). \tag{20}$$

For Be$^+$ the $S$ parameter has been calculated by King [35]. His value $S=0.452\,926\,3$ a.u. in combination with (17) give an estimate

$$\Delta E_{TIS}=0.0443\times10^{-6}\ E_H=292\ \text{MHz}. \tag{21}$$

The uncertainty of $\Delta E_{TIS}$ comes primarily from the King's $S$ parameter, which is converged to at most four significant figures. The TIS between $^9$Be and $^{10}$Be has been measured by Wen *at al.* [21] by means of the resonance-ionization mass spectroscopy. They reported $\Delta E_{TIS}=270\pm40$ MHz, which can be compared directly with (21).

### D. The magnetic properties

The nuclear magnetic shielding constant $\sigma$ and the magnetizability $\chi$ are, in general, tensor quantities composed of diamagnetic and paramagnetic parts. However, because of the spherical symmetry of the Be atom in $^1S$ state, the number of independent tensor components reduces to just one. The paramagnetic contribution is a second-order parameter and hence difficult to determine from a theoretical point of view. Another problem encountered in quantum-mechanical computations of $\sigma$ and $\chi$ is their gauge dependence. It originates from an incompleteness of the space spanned by a basis-set defining the wave function applied. The symmetry suggests a natural choice of the gauge origin—the position of the nucleus—for which the paramagnetic terms in $\sigma$ and $\chi$ vanish. Hence, both quantities have only first-order diamagnetic components expressed by the expectation values (in atomic units)

$$\sigma=\frac{4}{3c^2}\langle r_{en}^{-1}\rangle \tag{22}$$

and

$$\chi=-\frac{1}{3}\langle r_{en}^2\rangle. \tag{23}$$

We also believe that our high-quality wave function is able to produce practically gauge independent results.

The expectation value of the $r_{en}^{-1}$ operator extrapolated for $K=\infty$ and inserted to Eq. (22) yields the nuclear magnetic shielding constant,

$$\sigma=149.589\,28(4)\ \text{ppm}. \tag{24}$$

Similarly, the same wave function and Eq. (23) give

$$\chi=-1.353\,97(7)\ \text{a.u.}=-12.8683(6)\times10^{-6}\ \frac{\text{cm}^3}{\text{mol}}. \tag{25}$$

## IV. SUMMARY

The capability of producing very accurate results by the ECG functions has been proven many times for two- and three-electron systems [3–15]. This paper presents high-quality calculations on a four-electron system: the beryllium atom. It shows that the ECG functions are able to yield an energy converged up to 1 $\text{cm}^{-1}$. It exceeds the accuracy of any previous variational calculations by 1–2 orders of magnitude. The lowest variational upper bound to the ground-state energy of the nonrelativistic infinite-mass beryllium atom is $-14.667\,355E_H$. The energy predicted by an extrapolation amounts to $-14.667\,360(2)E_H$. Corresponding correlation energies are $-94.332\times10^{-3}E_H$ and $-94.337(2)\times10^{-3}E_H$, respectively.

At this moment the importance of the optimization procedure ought to be emphasized because it makes possible to speed up the convergence rate and apply shorter expansions of the wave functions. Already the energy obtained from our 150-term wave function is only about 38 $\text{cm}^{-1}$ in error, which is better than any other variational energy published to date. The comparison with the energy obtained from 150-term ECG of Schwegler *et al.* [36] reveals that the former yields an error over 25 times smaller. The other variational wave functions yielding energy close to that obtained with our 150-term function have several times larger expansion lengths ranging from 650 up to several thousands. The above shows the efficiency of our method also in applications where small basis sets have to be applied. In fact, the convergence acceleration comes from two equally important factors:

(a) The explicit inclusion of the interelectron distances into the basis function definition, Eq. (9);

(b) efficiently programed optimization algorithm.

The wave functions optimized with respect to the energy have been applied to evaluate expectation values of several operators. The easiness of evaluating integrals with Gaussian-type basis functions allowed us to compute a wide range of the expectation values of powers of distance operators as well as Dirac $\delta$, and the products of the nabla operators. These computations lead to highly accurate values of the magnetic shielding constant, $\sigma=149.589\,28(4)$ ppm, the magnetic susceptibility, $\chi=12.8683(6)\times10^{-6}$ $\text{cm}^3/\text{mol}$, the specific mass shifts, $\Delta E_{SMS}^{9Be}=28.0182(2)\times10^{-6}E_H$, $\Delta E_{SMS}^{10Be}=25.2159(2)\times10^{-6}E_H$ and the transition isotope shift, $\Delta E_{TIS}=293$ MHz. These values are the most accurate computed to date, and together with the ground-state energy could serve as a reference for these quantities.

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