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Reexamination of the calculation of two-center, two-electron integrals over Slater-type orbitals. III. Case study of the beryllium dimer

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In this paper we present results of *ab initio* calculations for the beryllium dimer with a basis set of Slater-type orbitals (STOs). Nonrelativistic interaction energy of the system is determined using the frozen-core full configuration interaction calculations combined with high-level coupled-cluster correction for inner-shell effects. We have developed STO basis sets, ranging in quality from double to sextuple ζ, which are used in these computations. Principles of their construction are discussed and several atomic benchmarks are presented. Relativistic effects of order α^2 are calculated perturbatively by using the Breit-Pauli Hamiltonian and are found to be significant. We also estimate the leading-order QED effects. Influence of the adiabatic correction is found to be negligible. Finally, the electronic binding energy of the beryllium dimer is determined to be $929.0 \pm 1.9\,\mathrm{cm}^{-1}$, in a very good agreement with the recent experimental value.

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I. INTRODUCTION

State-of-the-art *ab initio* electronic structure calculations are very important for the new emerging field at the border of chemistry and physics: the studies of ultracold molecules. During the past decades, experimental advances in laser cooling and trapping of neutral atoms have opened a door for the formation of ultracold diatomic molecules by photoassociation [1] and magnetoassociation [2] techniques. In this respect, *ab initio* calculations of the potential energy curves and coupling matrix elements between the electronic states turned out to be crucial to interpret the experimental observations. See, for instance, Ref. [3] for the theoretical explanation of the unusual quadratic Zeeman shifts in the Sr_2 molecule, or Ref. [4] for interpretation of the observed subradiant states of Sr_2. Electronic structure calculations can also be used to predict new schemes for the formation of ultracold diatomic molecules [5–9]. Apart from that, state-of-the-art first-principles calculations are used in metrology, e.g., to determine the pressure standard [10]. Last, but not least, accurate interatomic interaction potentials are of significant importance in search for a new physics. See, e.g., Ref. [11] for a theoretical study of the QED retardation effect of the helium dimer and the work of Zelevinsky *et al.* [12] for a joint experimental-theoretical effort towards determination of the proton-electron mass ratio time variation. Additionally, one can mention the work of Schwerdtfeger *et al.* [13] on the Sr_2 molecule where time variation of the fine structure constant is investigated.

All the aforementioned physical applications require high-precision theoretical data. Slater-type orbitals (STOs) are expected to improve the description of many-electron systems, thus leading to results more accurate than available at present. In the first two papers of the series we proposed efficient algorithms for the calculation of two-center integrals over STOs [14,15]. As the first application of the STO integral code we performed calculations for the beryllium dimer in its ground $^1\Sigma_g^+$ state. This is a challenging system, from both the theoretical and the experimental points of view. From the theory side, it has already been known that in order to reach accurate results, very advanced quantum chemistry methods must be used. In fact, probably the first calculations performed for this system by Fraga and Ransil [16], using the restricted Hartree-Fock (RHF) method, led to the conclusion that the potential energy curve is purely repulsive. Further inclusion of the electron correlation, by using the configuration interaction (CI) method with single and double substitutions (CISD), appeared to confirm this observation [17]. However, more refined calculations with the same method indicated an existence of a weak bond [18,19], with the interaction energy of the order of several tens of cm^{-1} and equilibrium distance of ≈ 5 Å, which is characteristic for the van der Waals molecules such as Ne_2. A similar conclusion was found in a study [20] employing the coupled-cluster (CC) methods with double (and single) excitations (CCD, CCSD).

However, somehow later Harrison and Handy [21] performed frozen-core full configuration interaction (FCI) calculations and found that the interaction energy is at least several hundreds of cm^{-1} larger. Even more importantly, they reported the presence of a deep minimum around 2.5 Å, which was a rather unexpected result at this time. These results indicate that the connected triple (and possibly also quadruple) excitations are responsible for the formation of the bond. Reasons for such slow convergence of the traditional CI or CC expansions were analyzed in detail by Liu and McLean [22]. It was shown that the pathological behavior of this system encountered during studies performed with the single reference methods is mostly due to near degeneracy of the $2s$ and $2p$ orbitals of the beryllium atom. It gives the beryllium dimer a strongly multireference nature. By applying the multireference configuration interaction (MRCI) method, Liu and McLean found the interaction energy to be as large as 810 cm^{-1} and confirmed the existence of the minimum around 2.5 Å. These findings were later verified by several independent MRCI studies [23–30]. Therefore, it is now well established that Be_2 is *not* a van der Waals molecule.

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Since then, a large number of theoretical works entirely devoted to study of the beryllium dimer have been published and a more detailed bibliography is given elsewhere [31,32]. The interaction energy is typically determined to be within the range of 200–1000 cm^{-1} and it varies with the level of theory and quality of the basis sets used. However, it appears that in the most recent, and probably the most accurate, studies, the interaction energy fluctuates somewhere around 900 cm^{-1}. For instance, Martin [33] found $944 \pm 25\,\mathrm{cm}^{-1}$, Gdanitz [34], 989 ± 8 cm^{-1}; Pecul *et al.* [35], $885\,\mathrm{cm}^{-1}$; Reggen and Veseth [31], $945 \pm 15\,\mathrm{cm}^{-1}$; Patkowski *et al.* [32], $938 \pm 15\,\mathrm{cm}^{-1}$; Koput [36], $935 \pm 10\,\mathrm{cm}^{-1}$; and Sharma *et al.*, 931.2 cm^{-1} [37]. Discrepancies between these results are still rather large, though, which indicates that the ground state of the beryllium dimer remains to be a challenge for modern quantum chemistry methods.

From the experimental point of view, the ground state of the beryllium dimer is also a demanding system. The first empirical confirmation of the fact that Be_2 is a deeply bound system, as theoretically predicted, was reported in the 1980s [38–40]. The most frequently cited experimental result for the well depth was given by Bondybey *et al.*, 790 ± 30 cm^{-1}. This result was not accurate and the true error is much larger than the estimated error bars. However, the discrepancy was not really due to the experimental error but mostly due to theoretical assumptions used to extract the dissociation energy. In fact, in 2006 Spirko [41] combined the experimental data of Bondybey with the best theoretical potential energy curve available at the time and refined the result to 923 cm^{-1}, which is much closer to the recent theoretical findings. In 2009 a new experiment was performed by Merritt *et al.* [42] and the interaction energy was found to be $929.7 \pm 2.0\,\mathrm{cm}^{-1}$. Additionally, 11 vibrational levels were characterized [43]. Shortly afterwards, Patkowski *et al.* [44] suggested the existence of the 12th vibrational level, just 0.44 cm^{-1} below the dissociation limit, by using the "morphed" theoretical potential energy curve.

It is clear that the ground state of the beryllium dimer is a challenging system, with large requirements for the quality of the basis set and for the theoretical methods. Therefore, it is a good test case for the STOs combined with the state-of-the-art quantum chemistry methods. It is well known that STOs are able to satisfy the electron-nucleus cusp condition, thereby significantly improving the description of the wave function in the vicinity of the nuclei. This property makes STOs more reliable in calculations which depend crucially on the quality of the trial wave function in this regime, such as core-core and core-valence correlation effects, one-electron relativistic corrections of order α^2, etc. Other advantages of STOs are summarized at the end of the present paper. Notably, calculations with STO basis sets of quality up to sextuple ζ, aiming at spectroscopic accuracy, have never been performed thus far. In the case of such calculations special attention must be paid to technical issues, such as creation and benchmarking of basis sets, since the strategies adopted in case of Gaussian-type orbitals (GTOs) may not be straightforwardly transferable. In this paper we consider these issues in some detail but restrict ourselves to calculations at the equilibrium internuclear distance, R, equal to 2.4536 Å, which is the recent experimental value [42]. The whole potential energy curve will be reported later, along with a detailed study of the related spectroscopical issues.

This paper is organized as follows. In Sec. II we describe in detail the systematic construction of the STO basis sets. In Sec. III we present benchmarks for the beryllium atom which verify the reliability of the developed STO basis sets. Issues connected with extrapolations towards the complete basis set (CBS) are also investigated. In Sec. IV we present results for the ground state of the beryllium dimer. We calculate the valence and core correlations effects separately and estimate the corresponding errors. Additionally, we compute the values of the relativistic corrections and estimate the effects of the leading-order QED contributions. Finally, in Sec. V we conclude the paper and give a short outlook.

II. BASIS SETS

In the case of GTOs, the contracted functions are typically used to reproduce the Hartree-Fock energy first. Then, additional uncontracted functions are used to describe the electronic correlation; see the works of Dunning *et al.* [45–53] as a representative example. We found that GTO basis sets designed according to this principle somewhat lack flexibility for the $l = 0$ partial wave, especially in the molecular environment, since the number of uncontracted $1s$ orbitals is typically small. For ordinary GTO calculations this is not a problem, however, because correlation energy retrieved by $l = 0$ angular momentum functions is small, at least an order of magnitude below the contribution from $l = 1$ partial wave. Therefore, this lack of correlation coming from $l = 0$ functions is visible only for very accurate calculations where the contributions from more important partial waves are already sufficiently saturated. Since we aim at high-quality results, we do not use contractions of STOs.

There is also another important choice in the design of STO basis sets which is entirely absent in the case of GTO. For GTO calculations one typically uses only $1s$, $2p$, $3d$, etc., functions (with $n = l + 1$) since molecular integrals with these kinds of functions are particularly straightforward. In the case of STO one can use functions with $n > l + 1$ as well. For instance, in the case of $l = 0$ orbitals the expansion takes the form

$$\psi_i = e^{-\zeta_i r} \sum_k^{N_i} c_{ki}\, r^k, \tag{1}$$

where the value of ζ_i is characteristic for a given atomic shell. The expansion (1) is quite attractive, mainly because of a small number of nonlinear parameters which need to be optimized, only one per atomic shell, and very systematic enlargement towards the completeness through the parameters N_i. However, in practice we found that there are numerous problems connected with this expansion in our applications. The biggest drawback is the fact that basis sets constructed according to the principle (1) suffer from near-linear dependencies when N_i gets moderate or large. This effectively prohibits the construction of large basis sets close to completeness when the standard double precision arithmetic is used. Another problem is the fact that the expansion (1) is not as flexible as necessary, especially when transferred from atomic to a weakly bound molecular system.

TABLE I. Composition of STO basis sets for the beryllium atom.

Basis set	Atomic valence	Tight core	Diffuse
ATC-ETCC-1	$6s1p$	$1s$	$1s1p$
ATC-ETCC-2	$7s2p1d$	$1s1p$	$1s1p1d$
ATC-ETCC-3	$8s3p2d1f$	$2s2p1d$	$1s1p1d1f$
ATC-ETCC-4	$9s4p3d2f1g$	$2s3p2d1f$	$1s1p1d1f1g$
ATC-ETCC-5	$9s5p4d3f2g1h$	$3s4p3d2f1g$	$1s1p1d1f1g1h$
ATC-ETCC-6	$9s6p5d4f3g2h1i$	$3s5p4d3f2g1h$	$1s1p1d1f1g1h1i$

As a result, we found that more flexible and well-behaved basis sets can be obtained when the orbitals are expanded, similarly as for GTO, in a set of functions with $n = l + 1$ and their respective exponents are varied freely, i.e.,

$$\psi_i = \sum_{k}^{N_i} c_{ki}\, e^{-\zeta_{ik} r}. \tag{2}$$

This choice, however, brings up the problem of optimization of a large number of independent parameters ζ_{ik}. In the biggest basis set created in this work a direct use of Eq. (2) would require free optimization of several tens of the nonlinear parameters. This is possible but very time consuming. An even more daunting problem is the presence of a great number of local minima. There is no guarantee that a brute-force optimization would have found the true global minimum, even with a decent starting point. This fact puts the reliability of the extrapolation towards the CBS in question.

Aware of all the aforementioned issues, we adopted the strategy of *even tempering* so that the nonlinear parameters for a given angular momentum l are in the following form:

$$\zeta_{lk} = \alpha_l\, \beta_l^k \quad \text{with} \quad k = 0,1,2,\ldots. \tag{3}$$

Nowadays, even tempering is routinely applied for construction of GTO basis sets. However, this technique was originally proposed by Raffenetti and co-workers [54,55] in the context of STOs. Even tempering greatly reduces the number of independent parameters which need to be optimized (only two for each partial wave).

The first step in the creation of the STO basis sets is optimization of the atomic valence basis set. In this step the core $1s$ orbital of the beryllium atom is kept frozen and the CISD method, equivalent to FCI for the valence shell, is used. The optimization is carried out to minimize the *total* energy of the two-electron CISD, i.e., sum of the Hartree-Fock and CISD correlation energy.

Since the seminal work of Dunning and co-workers [45–53] it has been known that to allow for a reliable extrapolation towards CBS, basis sets need to be constructed according to the *correlation consistency* principle. Roughly speaking, it ensures that at a given stage all functions which give approximately the same energy contributions are simultaneously included. Our atomic valence basis sets are denoted ETCC-L, which stands for even-tempered correlation consistent and L is the largest angular momentum included. Therefore, ETCC-1 has the composition $6s1p$, ETCC-2 $7s2p1d$, and so forth, and only functions with $n = l + 1$ are used. The initial number of six $1s$ functions was found to be optimal. Compositions of all basis sets up to $L = 6$ are presented in Table I. At some point it becomes unnecessary to include more $1s$ functions, and thereafter their number was kept fixed. The even-tempered expansion (3) is used separately for each partial wave.

The second step in construction of the basis set for beryllium is addition of the "tight" functions which are necessary for description of the core-core and core-valence correlations. It is well known that the core electrons are chemically inert and their contribution to the total energy cancels out to a large extent when interaction energies are computed. This observation is the foundation for the so-called frozen-core approximation. However, in accurate calculations the frozen-core approximation cannot be applied, especially for an element such as beryllium. Obviously, valence basis sets cannot describe the core-core and core-valence correlations since polarization functions with large exponents, characteristic for the core, are absent. We added core polarization functions to the previously obtained ETCC-L basis sets. Detailed composition of the extended TC-ETCC-L basis sets (where TC stands for "tight core") is given in Table I for each L. In order to optimize the exponents of the core polarization functions, we minimized the difference between the total energies of all-electron CISD and frozen-core CISD for the beryllium atom. Since the number of independent nonlinear parameters was much smaller than for the valence basis sets, even tempering of the exponents was not necessary and all variables were optimized freely. A minor detail of the optimization procedure is that the derivative of the target function with respect to the logarithm of the exponent was used as a gradient, rather than the derivative with respect to the exponent itself. This stabilizes greatly the numerical performance of the optimization.

The third, and final, step of the basis sets creation is the addition of the diffuse functions. These functions are not necessary for the atomic calculations since tails of the electron density do not contribute greatly to the total energies of the atom. However, in a molecular environment tails of the electron density are responsible for the act of bonding in weakly interacting systems and accurate reproduction of the potential energy curve. Basis sets augmented with a set of diffuse functions are called A-ETCC-L, or ATC-ETCC-L in the case of the core-valence basis sets. A detailed structure of the augmented basis sets is given in Table I. Exponents of the diffuse functions were optimized to maximize the absolute value of the beryllium dimer interaction energy calculated with A-ETCC-L basis sets at the four-electron (valence) CCSD(T) level of theory [56].

Notably, the strategy that the diffuse functions are optimized to maximize the absolute value of the interaction energy makes them formally dependent on the internuclear distance, R. This is, in fact, exactly in line with our intentions. In this work we consider only one value of R, corresponding to the minimum of the potential energy curve, so that there is no ambiguity in how the calculations are carried out. In a case where a complete potential energy curve is required, diffuse functions can be optimized for several values of R and then interpolated smoothly. The present approach is inspired by the works of Kołos and co-workers concerning the hydrogen molecule [57–60]. Basis sets used in these works contained several nonlinear parameters which were handled in a manner similar to that described above and no significant difficulties were reported.

All optimizations necessary to construct the basis sets were carried out by using a pseudo-Newton-Rhapson method with an approximate update of the Hessian matrix [61]. Our own code, written especially for this purpose, was used throughout. This program is interfaced with the GAMESS package [62,63], which carries out the electronic structure calculations. A gradient with respect to nonlinear parameters was calculated numerically with the two-point finite difference formula. Close to a minimum, where more accurate values of the gradient are necessary, the four-point finite difference formula was applied. Optimization was stopped when the energy differences between two consecutive iterations fell below 1 nH and the largest element of the gradient fell below 10 μH, simultaneously. Typically, several tens of iterations were necessary to converge to a minimum in the biggest calculations. To avoid the exponent values of two functions collapsing, which occasionally happened, a Gaussian-type penalty function was applied routinely.

STOs constitute a convenient basis set for calculation of the relativistic corrections because of the cusp at the origin. Nonetheless, it is obvious that standard STO basis sets used in calculation of the Born-Oppenheimer potential may not be fully satisfactory. To overcome this problem we modified our ATC-ETCC-L basis sets by replacing all $1s$ orbitals with a new set, common for each L. The latter consists of 15 functions and was trained to minimize the Hartree-Fock energy of the beryllium atom. The value obtained, −14.573 023 138 5, differs at the 10th significant digit from the best estimate available in the literature, −14.573 023 168 305 [64]. The s-extended basis sets are abbreviated as ATC-ETCC-L+S.

Composition of the STO basis sets along with detailed values of the exponents and quantum numbers are given in the Supplemental Material [65].

III. ATOMIC BENCHMARKS

A. Nonrelativistic energy

The beryllium atom is a convenient system for benchmarking purposes because accurate reference values of the total energies and relativistic corrections are available in the literature. Therefore, before the calculations on the diatomic system are given, it is useful to check the adequacy of the strategy and the performance of our basis sets in the atomic case. We calculated the FCI energies of the beryllium atom by using ATC-ETCC-L basis sets with $L = 2, \ldots, 6$. A general FCI program HECTOR [66], written by one of us (M.P.), was used for this purpose. The starting Hartree-Fock orbitals were taken from the GAMESS program package, interfaced with our STO integral code.

TABLE II. Total energy, E_{total}, and the correlation energy, E_c, of the beryllium atom calculated at the FCI level of theory by using the STO basis sets ATC-ETCC-L. The limit of the Hartree-Fock energy is assumed to be -14.573 023 H.

Basis set	E_c/mH	E_{total}/H
ATC-ETCC-2	−85.976	−14.658 998
ATC-ETCC-3	−91.479	−14.664 502
ATC-ETCC-4	−92.994	−14.666 017
ATC-ETCC-5	−93.608	−14.666 631
ATC-ETCC-6	−93.902	−14.666 925
CBS	−94.322	−14.667 345
Pachucki and Komasa [71]	−94.333	−14.667 356

In Table II we present the FCI results for the beryllium atom. It is important for further developments to extrapolate these results towards the CBS limit. Many extrapolation methods were suggested in the literature [67–70], but the following formula was found to be particularly reliable for the estimation of the CBS limit of the correlation energy,

$$E = A + \frac{B}{L^3} + \frac{C}{L^5}, \tag{4}$$

where L is the largest angular momentum present in the basis set. The Hartree-Fock results were not extrapolated but simply the value in the biggest basis set was taken. Extrapolation of the results given in Table II leads to the result −14.667 345 for the total energy of the beryllium atom. This can be compared with the reference value, obtained by Pachucki and Komasa [71] by using an explicitly correlated four-electron basis set, −14.667 356, and the error is equal to 11 μH. Remarkably, the extrapolation reduces the error by an order of magnitude, compared with the largest basis set available. In fact, we found that an essential feature of STO basis sets is that they provide very reliable extrapolation towards the CBS limit, as compared with GTO basis sets of a similar quality.

B. One-electron relativistic corrections

The leading relativistic corrections (the second order in the fine structure constant, α) to the energy of light systems can be computed perturbatively as an expectation value of the Breit-Pauli Hamiltonian [72]. For a molecule in a singlet state, this correction is [73,74]

$$E^{(2)} = \langle P_4 \rangle + \langle D_1 \rangle + \langle D_2 \rangle + \langle B \rangle, \tag{5}$$

$$\langle P_4 \rangle = -\frac{\alpha^2}{8} \left\langle \sum_i \nabla_i^4 \right\rangle, \tag{6}$$

$$\langle D_1 \rangle = \frac{\pi}{2}\alpha^2 \sum_a Z_a \left\langle \sum_i \delta(\mathbf{r}_{ia}) \right\rangle, \tag{7}$$

$$\langle D_2 \rangle = \pi\alpha^2 \left\langle \sum_{i>j} \delta(\mathbf{r}_{ij}) \right\rangle, \tag{8}$$

$$\langle B \rangle = \frac{\alpha^2}{2} \left\langle \sum_{i>j} \left[\frac{\boldsymbol{\nabla}_i \cdot \boldsymbol{\nabla}_j}{r_{ij}} + \frac{\mathbf{r}_{ij} \cdot (\mathbf{r}_{ij} \cdot \boldsymbol{\nabla}_j)\boldsymbol{\nabla}_i}{r_{ij}^3} \right] \right\rangle, \tag{9}$$

where $\langle \hat{O} \rangle = \langle \Psi | \hat{O} | \Psi \rangle$. The consecutive terms in the above expression are the mass-velocity $\langle P_4 \rangle$, one-electron Darwin $\langle D_1 \rangle$, two-electron Darwin $\langle D_2 \rangle$, and Breit $\langle B \rangle$ corrections, respectively. We assume that the value of the fine structure constant, α, is $1/137.035\,999\,7$, as recommended by CODATA [75].

Let us consider the values of the one-electron relativistic corrections, $\langle P_4 \rangle$ and $\langle D_1 \rangle$. They can easily be obtained within the STO framework, since the corresponding one-electron integrals are fairly straightforward to compute. Integrals including the one-electron Dirac δ distribution reduce to the values of STOs at a given point of space which is elementary. Integrals including the ∇^4 operator reduce to combinations of the ordinary overlap integrals over STOs. General subroutines for calculation of the aforementioned integrals are now a part of our STO integral package. Note that $\langle P_4 \rangle$ and $\langle D_1 \rangle$ corrections (called also collectively the Cowan-Griffin contribution [76]) are very sensitive to the quality of the wave function in the vicinity of the nuclei. Therefore, their evaluation by using the STO basis set is supposed to be particularly advantageous.

In Table III we present values of the one-electron relativistic corrections, calculated with s-extended STO basis sets. The results are compared with the values reported recently [71], which are considered "exact" in the present context. Remarkably, in the biggest basis set, ATC-ETCC-6+S, the relative error of our values compared with the accurate ones is only ≈0.03% and ≈0.003% for $\langle P_4 \rangle$ and $\langle D_1 \rangle$, respectively. Moreover, even in the smallest basis set, ATC-ETCC-2+S, these errors increase to only about 0.1% and 0.005%. We found that it is impossible to reach a similar level of accuracy with the available (decontracted) GTO basis sets, and typically the resulting error is (at least) an order of magnitude larger.

It is also interesting to perform extrapolations of the values of one-electron relativistic corrections towards CBS. We found empirically that the following formulas provide the best fit:

$$A + \frac{B}{(L+1)^2} \quad \text{for} \quad P_4, \tag{10}$$

$$A + \frac{B}{(L+1)^4} \quad \text{for} \quad D_1. \tag{11}$$

Results of the extrapolations from $L = 3, 4, 5, 6$ are presented in Table III. The extrapolation reduces the error of the mass-velocity correction to 0.02%, but increases it insignificantly for the one-electron Darwin correction.

TABLE III. Mass-velocity, $\langle P_4 \rangle$, and one-electron Darwin, $\langle D_1 \rangle$, corrections for the beryllium atom at the FCI level of theory. The factor of α^2 is not included. All values are given in atomic units.

Basis set	$\langle P_4 \rangle$	$\langle D_1 \rangle$
ATC-ETCC-2+S	−270.431 854	222.218 606
ATC-ETCC-3+S	−270.527 702	222.225 660
ATC-ETCC-4+S	−270.568 886	222.232 142
ATC-ETCC-5+S	−270.594 238	222.234 514
ATC-ETCC-6+S	−270.609 955	222.235 299
CBS	−270.648 568	222.236 568
Pachucki and Komasa [71]	−270.704 68(25)	222.229 35(13)

IV. BERYLLIUM DIMER

A. Four-electron (valence) contribution

From earlier studies of the beryllium dimer, it is well known that a major contribution to the interaction energy comes from the correlations between valence electrons. Freezing both $1s$ atomic orbitals makes the dimer effectively a four-electron system which can be successfully treated with FCI method in large basis sets. We performed the frozen-core FCI calculations in basis sets A-ETCC-L with $L = 2, \ldots, 6$. The Abelian group, D_{2h}, was used in computations. We believe these are the biggest valence FCI calculations ever performed for this system in terms of the number of configurations included in construction of the Hamiltonian matrix. The results of the calculations are included in Table IV. In all cases the counterpoise (CP) correction for the basis set superposition error (BSSE) was applied [77]. It is clear, that the results are slowly convergent with respect to the quality of the basis set. This is probably due to the fact that bonding significantly perturbs the atomic densities. The increment of the interaction energy between $L = 5$ and $L = 6$ basis sets is as large as $11.9\ \text{cm}^{-1}$, suggesting that the CBS value is still significantly below the $L = 6$ value.

Because of this observation it is necessary to perform some kind of extrapolation towards the CBS. The correlation energy alone was the subject of the extrapolation, separately for the atom and for the dimer. We used the formula (4) which was previously used successfully for the atomic calculations. We also observe that in the largest basis set, the Hartree-Fock (HF) results are already converged at least to eight significant digits. It is therefore unnecessary to extrapolate the HF results and simply the value obtained in $L = 6$ basis was taken as the CBS result.

Note that the CBS increment found in the extrapolation of the correlation energy is quite substantial and crucial for the final results. It amounts to as much as nearly $20\ \text{cm}^{-1}$ in the interaction energy. Thus, it is necessary to additionally verify the reliability of the extrapolation. To do so, we first performed the extrapolation from $L = 2, 3, 4, 5$ basis sets in order to estimate the $L = 6$ value. The extrapolated $L = 6$ value gives the interaction energy equal to $847.4\ \text{cm}^{-1}$, whereas the corresponding true calculated result is $845.7\ \text{cm}^{-1}$. The difference, amounting to $1.7\ \text{cm}^{-1}$, is assumed to be also the error of the CBS extrapolation from $L = 2, 3, 4, 5, 6$. The quality of the extrapolation for the dimer is illustrated at Fig. 1. A quite similar excellent fit was obtained for the atomic calculations. Finally, our best estimate for the valence contribution to the interaction energy is $864.9 \pm 1.7\ \text{cm}^{-1}$. Note that this error estimation is a conservative one because extrapolation from a larger number of points can be expected to be more reliable. Additionally, the increment in the interaction energy between $L = 4$ and $L = 5$ basis sets is significantly larger than between $L = 5$ and $L = 6$ or between $L = 6$ and the estimated CBS. Therefore, it is possible that our extrapolated result is more accurate than we assume here.

TABLE IV. Results of the four-electron valence FCI calculations for the beryllium dimer at the internuclear distance 2.4536 Å. N_b denotes the number of basis set functions, N_{SD} is the dimension of the Hamiltonian matrix in A_g symmetry, E_{HF} is the Hartree-Fock energy, E_c is the correlation energy at FCI level, CP is the CP correction (for BSSE) to the interaction energy, and D_e is the calculated CP-corrected FCI interaction energy. The values in the last row are the extrapolated CBS values (see the main text for the discussion). All values are given in the atomic units unless stated otherwise.

Basis set	N_b	N_{SD}	E_{HF}	E_c	CP (cm^{-1})	D_e (cm^{-1})
A-ETCC-2	54	237 548	−29.133 941 8	−0.104 687 3	12.5	273.8
A-ETCC-3	100	2 895 037	−29.134 162 1	−0.107 057 4	8.3	710.6
A-ETCC-4	168	23 685 257	−29.134 174 5	−0.107 639 2	4.1	802.9
A-ETCC-5	260	138 002 229	−29.134 175 1	−0.107 850 5	2.6	833.8
A-ETCC-6	384	663 593 429	−29.134 175 4	−0.107 942 3	1.8	845.7
CBS	∞	∞	−29.134 175 4	−0.108 069 5	0.0	864.9 ± 1.7

Our final result, namely 864.9 ± 1.7 cm^{-1}, is in line with recent findings of other authors. Patkowski *et al.* [32] found 857 ± 12 cm^{-1}, if we follow their method of error estimation, and Martin [33] gives 872 ± 15 cm^{-1}. The present result lies well within the error bounds obtained in these works. A slight discrepancy is found between our result and the value recently reported by Evangelisti and co-workers [78], who give 850.4 cm^{-1} without any error estimation. We believe that this result is inaccurate, mainly because lack of the diffuse functions in their GTO basis set. Notably, our error bounds, which are conservative anyway, are an order of magnitude smaller than those obtained in the aforementioned works.

B. Core-core and core-valence contributions

The second step in our calculations is a reliable determination of the core-core and core-valence contribution to the interaction energy. This task, however, is far from being trivial. A brief inspection of values available in the literature reveals that estimations from 65 cm^{-1} [78] to as large as 89 cm^{-1} [31] were obtained. Because of the fulfillment of the nuclear cusp condition, the STO basis used in the present work can be expected to be more suitable for the description of core region than the GTOs used thus far.

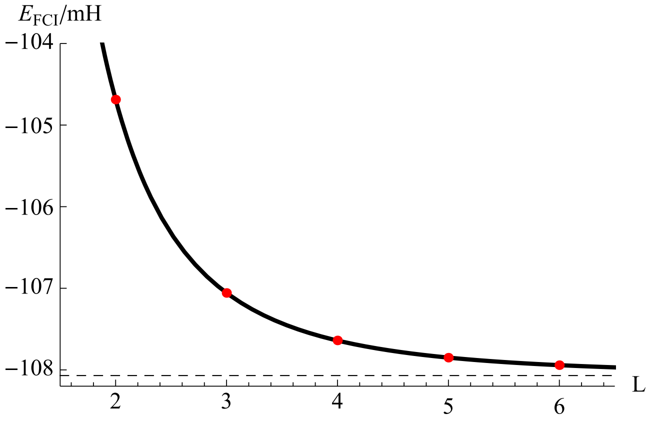

FIG. 1. (Color online) Quality of the extrapolation towards the CBS for the beryllium dimer using results from basis sets A-ETCC-L with $L = 2, \ldots, 6$ based on the theoretical expression (4). The dashed line denotes the estimated limit.

Our preliminary study suggests that the CCSDT model is a particularly good method for the estimation of the inner-shell contribution. The effect of connected quadruple excitations was found to be very small in this case. In fact, the effect of quadruples can be highly overestimated in small basis sets but quickly diminishes when the basis set is enlarged. We found this particular behavior in virtually any approximate quadruples method that was available to us. Therefore, we can conclude that the CCSDT method in the CBS limit would probably give the core-core and core-valence contribution accurate to within a few tenth of cm^{-1}. A similar observation was also made implicitly by Martin [33].

Unfortunately, we are able to perform all-electron CCSDT calculation only in ATC-ETCC-L basis sets with $L = 2$, 3, 4. The results are 31.5, 56.7, and 63.9 cm^{-1}, respectively. CBS extrapolation from these values can be performed by using formula (4), giving 69.6 cm^{-1}. However, this three-point extrapolation is not particularly trustworthy since the CBS increment is rather large and no reliable error estimation can be given. Thus, we must seek some approximate method, with smaller computational costs, giving results comparable to CCSDT in the CBS limit.

In Table V we show inner-shell contributions to the interaction energy computed at various levels of theory. CCSD, CCSD(T), and MP2 calculations were performed with the GAMESS package, while CCSDT and MP4 energies were evaluated with the help of the ACESII program [79]. All values in this table were obtained by subtracting the interaction energy obtained with the frozen-core approximation from the corresponding all-electron values. Let us compare the results of MP4 and CCSD(T) with the complete CCSDT model. One sees that the MP4 method slightly underestimates the inner-shell

TABLE V. Core-core and core-valence contributions to the interaction energy computed at various levels of theory. All values are given in cm^{-1}. Extrapolations are performed according to formula (4), for the atom and dimer separately, using the CP-corrected data.

Basis set	N_b	CCSD	CCSDT	CCSD(T)	MP2	MP4
ATC-ETCC-2	62	28.2	31.5	39.0	−34.0	28.9
ATC-ETCC-3	126	50.4	56.7	61.2	57.2	56.4
ATC-ETCC-4	224	55.7	63.9	66.4	63.6	63.5
ATC-ETCC-5	364	57.4		67.7	65.7	65.7
CBS	∞	59.3	69.6	69.5	67.8	68.4

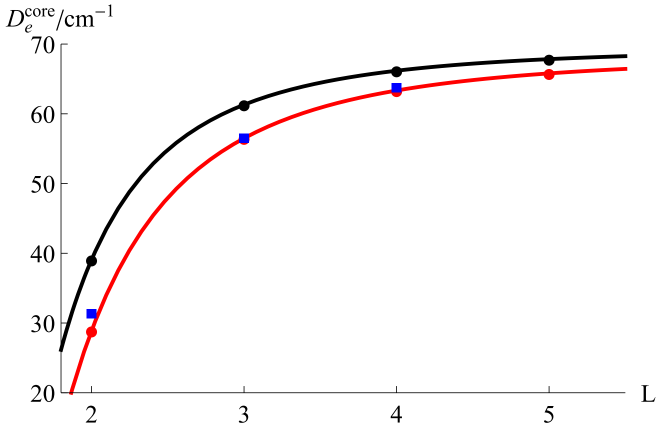

FIG. 2. (Color online) Contribution of the inner-shell effects to the interaction energy, denoted shortly $D_e^{\rm core}$, calculated by using ATC-ETCC-*L* basis sets. Black dots are the CCSD(T) results and the black line is the CCSD(T)/CBS extrapolation curve. Analogously, red dots are the MP4 results and the red line is the corresponding CBS extrapolation. Blue squares are the available CCSDT results, for $L = 2, 3, 4$.

contribution compared to CCSDT while the CCSD(T) model overestimates it significantly, especially in smaller basis sets. Note additionally that MP4 and CCSD(T) results strictly bracket the CCSDT values, as illustrated in Fig. 2. If we assume that this behavior holds further, then the CBS limit of the CCSDT method should lie between the corresponding limits of MP4 and CCSD(T). Fortunately, the CBS limit is 68.4 and 69.5 cm^{-1} for MP4 and CCSD(T), respectively. The exact result probably lies between these values so as the final result we take the average of the two and estimate the error as a half of the difference between them. This gives the final value of the core-core and core-valence contributions to the interaction energy equal to 69.0 ± 0.6 cm^{-1}. The small effect of the connected quadruples contribution is probably already incorporated in the error estimation.

Note that the final value determined by us is significantly smaller than some of the estimations given in the literature. For instance, Martin gives 76.2 cm^{-1} [33], while Patkowski *et al.* [32] reports as much as 85 ± 5 cm^{-1}. We believe that these discrepancies are mainly due to defects in the GTO basis sets used by authors. In fact, when GTO basis sets are not designed very carefully in the core region, the inner-shell correlation effects can be significantly overestimated. Naturally, STOs are much more appropriate in this respect, which is one of their noteworthy advantages.

C. Relativistic, QED, and adiabatic corrections

One-electron relativistic corrections were evaluated by using the s-extended basis sets, described in Sec. II. The results are presented in Table VI. Calculations of the one-electron expectation values, at the all-electron and frozen-core CCSD level of theory, were performed by using a Λ operator technique [80–83] implemented by default in the GAMESS package. Relaxation of the HF orbitals is neglected in CCSD calculations. FCI calculations were done using our own program and the expectation values are straightforward to evaluate by using the FCI wave functions.

Extrapolations are carried out by using the empirical formula (10) for *both* $\langle D_1 \rangle$ and $\langle P_4 \rangle$. Our strategy for evaluation of the contribution to the interaction energy from the Cowan-Griffin approximation [76] is as follows. We use the valence FCI values corrected for the core-core and core-valence effects as a difference between all-electron and frozen-core CCSD results. It was found previously that CCSD method behaves reasonably for the inner-shell correlations (see Table V) and this accuracy is sufficient for the present purposes. In Table VII we present contributions to the interaction energy from $\langle D_1 \rangle$ and $\langle P_4 \rangle$ corrections, calculated at this level of theory. The core-core and core-valence CCSD effect is estimated to be -0.4 cm^{-1}, while the pure valence FCI contribution is -4.4 cm^{-1}. By summing both corrections we obtain -4.8 ± 0.2 cm^{-1} for the final contribution to the interaction energy coming from the one-electron relativistic corrections. The error is simply taken as the (rounded up) value of the corresponding CBS increment. The obtained value is in a moderate agreement with the values given by Patkowski *et al.* [32], -4.1 cm^{-1}, Martin [33], -4.0 cm^{-1}, and Gdanitz [34], -5.2 cm^{-1}. However, as far as we can tell, these values are not extrapolated and the authors report no respective error bars of their result. We believe that our final values are much more accurate due to the fact that STO basis sets were used throughout.

Let us now focus on the two-electron relativistic corrections: two-electron Darwin, $\langle D_2 \rangle$, and Breit, $\langle B \rangle$, contributions. Evaluation of the latter correction within the STO basis set is not feasible at present. This is mostly due to the fact the matrix elements of the Breit term, Eq. (5), are extremely difficult to compute with the exponential functions. As far as we know, the only accurate molecular calculations of the Breit

TABLE VI. Mass-velocity, $\langle P_4 \rangle$, and one-electron Darwin, $\langle D_1 \rangle$, corrections for the beryllium dimer calculated at the CCSD and FCI levels of theory. The factor of α^2 is not included. All values are given in the atomic units.

	All-electron CCSD		Frozen-core CCSD		Frozen-core FCI	
Basis set	$\langle P_4 \rangle$	$\langle D_1 \rangle$	$\langle P_4 \rangle$	$\langle D_1 \rangle$	$\langle P_4 \rangle$	$\langle D_1 \rangle$
ATC-ETCC2+S	−539.847 891	443.692 152	−537.394 631	443.278 203	−537.133 303	443.083 762
ATC-ETCC3+S	−539.971 064	443.675 656	−537.333 536	443.241 928	−537.036 087	443.021 849
ATC-ETCC4+S	−540.030 590	443.664 899	−537.317 658	443.233 044	−537.014 183	443.008 427
ATC-ETCC5+S	−540.073 538	443.665 227	−537.310 464	443.229 426	−537.004 508	443.003 144
CBS	−540.141 465	443.655 919	−537.305 424	443.226 021	−536.995 150	442.996 653

TABLE VII. Contributions to the interaction energy of the beryllium dimer from the mass-velocity, $\langle P_4\rangle$, and one-electron Darwin, $\langle D_1\rangle$, corrections calculated at the CCSD and FCI levels of theory. All results are given in cm^{-1}.

	All-electron CCSD			Frozen-core CCSD			Frozen-core FCI		
Basis set	$D_e(P_4)$	$D_e(D_1)$	ΣD_e	$D_e(P_4)$	$D_e(D_1)$	ΣD_e	$D_e(P_4)$	$D_e(D_1)$	ΣD_e
ATC-ETCC2+S	−12.40	9.28	−3.12	−11.87	8.87	−3.00	−14.93	11.14	−3.78
ATC-ETCC3+S	−13.35	9.79	−3.57	−12.71	9.41	−3.30	−16.19	11.98	−4.21
ATC-ETCC4+S	−13.63	10.08	−3.54	−12.94	9.56	−3.38	−16.49	12.18	−4.30
ATC-ETCC5+S	−13.72	10.14	−3.58	−13.03	9.61	−3.42	−16.60	12.25	−4.35
CBS	−14.26	10.44	−3.81	−13.10	9.67	−3.44	−16.73	12.34	−4.39

term within the exponential basis set were performed by Kołos and Wolniewicz [59,84] for various electronic states of H_2.

Because of these difficulties, we calculated $\langle D_2\rangle$ and $\langle B\rangle$ in GTO basis sets. It will be shown that contributions of the two-electron relativistic corrections are small and GTO basis sets are sufficient to meet the prescribed accuracy requirements.

For calculations of the two-electron relativistic corrections we used modified aug-cc-pCVXZ series of GTO basis sets [45–53]. To improve the quality of the wave function the standard set of 1*s* GTO orbitals was replaced with a new one comprising 23 1*s* functions. This set was obtained by minimizing the HF energy of the beryllium atom. Apart from that, the original 1*s* diffuse functions from the initial aug-cc-pCVXZ basis sets were kept. We also decontracted the 2*p* polarization functions and removed the redundant orbitals. Higher angular momentum shells were neither modified nor decontracted.

The DALTON program package [85] was used for CCSD(T) calculations and our own program for the valence FCI calculations. In Table VIII we show contributions of $\langle D_2\rangle$ and $\langle B\rangle$ to the interaction energy computed at three different levels of theory: all-electron and frozen-core CCSD(T) and frozen-core FCI. It is not necessary to perform CBS extrapolations since the contributions to the interaction energy are converged to about 0.01–0.02 cm^{-1} already in the biggest basis set. We take the frozen-core FCI contribution as our result and additionally correct it for the inner-shell effects as a difference between the all-electron and frozen-core CCSD(T) values. In this way, we obtain the contribution to the interaction energy from the two-electron relativistic correction equal to –0.5 cm^{-1}. The error can be estimated to be much below 0.1 cm^{-1} by observing the convergence pattern in the available basis sets. Unfortunately, we are not aware of any available literature values that we could compare with.

By summing the computed one- and two-electron relativistic contributions, we find that α^2 effects decrease the interaction energy by 5.3 ± 0.2 cm^{-1}. This contribution is quite sizable and definitely needs to be included to obtain a spectroscopically accurate potential energy curve for the beryllium dimer.

Let us now pass to the leading-order QED contribution. Theoretically, this effect should be by a factor α smaller than the Breit-Pauli contribution and thus entirely negligible within the present accuracy requirements. However, it turns out that among the relativistic contributions to the interaction energy there is a significant cancellation between $\langle P_4\rangle$ and $\langle D_1\rangle$ terms, so that the result is an order of magnitude smaller than the net values of separate terms. Therefore, the leading QED corrections may still contribute to the interaction energy significantly. In fact, this situation was previously encountered in calculations for the dihydrogen [86] and the helium dimer [87]. This suggests that whenever the α^2 relativistic corrections are included in accurate calculations for light systems, the leading-order QED contributions should also be at least estimated.

The leading QED correction (of the order α^3 and $\alpha^3\ln\alpha$) to the electronic energy of a molecular singlet state takes the form [88,89]

$$E^{(3)} = \frac{8\alpha}{3\pi}\left(\frac{19}{30} - 2\ln\alpha - \ln k_0\right)\langle D_1\rangle + \frac{\alpha}{\pi}\left(\frac{164}{15} + \frac{14}{3}\ln\alpha\right)\langle D_2\rangle + \langle H_{\mathrm{AS}}\rangle, \qquad (12)$$

where $\ln k_0$ is the so-called Bethe logarithm [72,90] and $\langle D_1\rangle$ and $\langle D_2\rangle$ are the values of the one- and two-electron Darwin corrections (including the factor of α^2). The term $\langle H_{\mathrm{AS}}\rangle$ is the Araki-Sucher contribution, given by the expectation value

$$\langle H_{\mathrm{AS}}\rangle = -\frac{7\alpha^3}{6\pi}\left\langle \sum_{i>j}\hat{P}\left(r_{ij}^{-3}\right)\right\rangle, \qquad (13)$$

TABLE VIII. Contributions to the interaction energy of the beryllium dimer from the two-electron Darwin, $\langle D_2\rangle$, and Breit, $\langle B\rangle$, corrections calculated at the CCSD(T) and FCI levels of theory within GTO basis sets. All results are given in cm^{-1}.

	All-electron CCSD(T)			Frozen-core CCSD(T)			Frozen-core FCI		
Basis set	$D_e(D_2)$	$D_e(B)$	ΣD_e	$D_e(D_2)$	$D_e(B)$	ΣD_e	$D_e(D_2)$	$D_e(B)$	ΣD_e
aug-cc-pCVDZ	0.38	−0.82	−0.44	0.41	−0.73	−0.32	0.42	−0.76	−0.34
aug-cc-pCVTZ	0.42	−0.89	−0.47	0.46	−0.77	−0.32	0.46	−0.80	−0.34
aug-cc-pCVQZ	0.43	−0.90	−0.47	0.47	−0.79	−0.31	0.48	−0.82	−0.34
aug-cc-pCV5Z	0.44	−0.91	−0.47	0.48	−0.79	−0.31	0.48	−0.82	−0.34

and $\hat{P}(r_{ij}^{-3})$ denotes the regularized r_{ij}^{-3} distribution

$$\langle \hat{P}(r_{ij}^{-3}) \rangle = \lim_{a\to 0} \langle \theta(r_{ij}-a) r_{ij}^{-3} + 4\pi(\gamma_E + \ln a)\delta(\mathbf{r}_{ij}) \rangle, \quad (14)$$

where γ_E is the Euler-Mascheroni constant. It is well known that computation of the Bethe logarithm and Araki-Sucher terms is extremely difficult and has never been attempted for any molecular system apart from the dihydrogen [86] and the helium dimer [87]. Therefore, we have to adopt some approximate strategy for determination of $E^{(3)}$. Fortunately, except at very large R, the Araki-Sucher term is small compared to the overall leading-order QED correction and thus can be neglected. The Bethe logarithm, on the other hand, was found to vary insignificantly as the function of R, when R is moderate (or large), for the helium dimer and dihydrogen. Therefore, the asymptotic (atomic) value of the Bethe logarithm can be adopted.

A very accurate value of $\ln k_0$ for the beryllium atom has been given recently by Pachucki and Komasa [71], $\ln k_0 = 5.750\,34$. We use the extrapolated values of $\langle D_1 \rangle$ and $\langle D_2 \rangle$, equal to 0.023 613 and 0.000 522 for the dimer and 0.011 836 and 0.000 262 for the monomer, respectively. With these assumptions, contribution of the lowest-order QED effects to the interaction energy of the beryllium dimer is calculated to be 0.37 cm^{-1}. This value is an order of magnitude smaller than the relativistic corrections, as expected. However, its omission would significantly increase the total error of our theoretical predictions. It is difficult to estimate strictly what is the effect of the adopted approximations on the value of QED contribution to the interaction energy. For the dihydrogen molecule, exactly the same approximations introduce an error slightly less than 10%, based on the results presented in Ref. [86]. Therefore, we can assume very conservatively that error of the present calculations is at most 20%. This finally gives us estimation of the leading-order QED contribution to the interaction energy equal to 0.4 ± 0.1 cm^{-1}.

We also check the next higher-order QED contribution. It is well known from the calculations on the helium atom [91,92], that the α^4 effects are dominated by the one-loop term [93] given by

$$E^{(4)}_{\text{one-loop}} = 16\alpha^2 \left(\frac{427}{192} - \ln 2 \right) \langle D_1 \rangle, \quad (15)$$

in the case of the beryllium atom (or dimer). The above quantity is a scaled one-electron Darwin correction and thus can be easily computed. We found the contribution to the interaction energy of the one-loop term to be approximately 0.017 cm^{-1}, which is well below 0.1 cm^{-1}. Therefore, as anticipated, the higher-order QED contributions can safely be neglected within the present accuracy requirements. This additionally gives a verification that the QED perturbative series converges rapidly for the beryllium dimer.

The remaining missing part of the theory that has to be investigated is the finite nuclear mass, i.e., the adiabatic correction. We calculated this correction with help of the CFOUR [94] and MRCC [95,96] program packages at both all-electron and frozen-core CCSD and CCSDT levels of theory [97]. The GTO basis sets which were previously used for computation of the two-electron relativistic corrections were utilized. In all cases we found that the contribution to the interaction energy from the adiabatic correction was significantly below 0.1 cm^{-1}. In fact, the net values of the adiabatic correction for both atom and dimer were large, but they canceled out almost to zero. This is probably due to the fact that the adiabatic correction contribution to the interaction energy as a function of the internuclear distance, R, crossed zero near the value of R adopted by us (close to the minimum). A similar situation was found in the case of the helium dimer [87]. Our observation is additionally verified by calculations of Koput [36], who found that contribution of the adiabatic correction to the interaction energy varies by only 2 cm^{-1} along the whole potential energy curve. As a result, we assume that the contribution to the interaction energy coming from the adiabatic effects is equal to zero. We estimate that the error of this result is at most 0.1 cm^{-1}.

TABLE IX. Final error budget of the calculations for the ground state ($^1\Sigma_g^+$) of the beryllium dimer obtained in this work. All values are given in cm^{-1}.

	Contribution to D_e
Valence correlations	+864.9 ± 1.7
Inner-shell correlations	+69.0 ± 0.6
Relativistic (α^2) effects	−5.3 ± 0.2
Leading-order (α^3) QED effects	+0.4 ± 0.1
Adiabatic correction	+0.0 ± 0.1
Total	+929.0 ± 1.9
Experiment	+929.7 ± 2.0

D. Total interaction energy

All contributions to the interaction energy of the beryllium dimer computed in this work are listed in Table IX. By summing all contributions we obtain the value 929.0 cm^{-1}, which is the main result of our study. The overall error of the calculations is estimated by summing squares of all fractional errors (1.7, 0.6, 0.2, 0.1, 0.1 cm^{-1}) and taking the square root, which gives 1.9 cm^{-1} (rounded up) or 0.2%. The total result, 929.0 ± 1.9 cm^{-1}, is in very good agreement with the latest experimental value, 929.7 ± 2.0 cm^{-1}, reported by Merritt *et al.* [42]. In fact, the present result lies within the error bars of the empirical value and *vice versa*.

Let us also comment on the timings of the present calculations. It is true that any gain connected with the use of STOs can easily diminish if computation of the STO two-electron integral files becomes overwhelmingly time consuming, up to a point when it is more expensive than evaluation of the correlation energy. There is such a risk, because STO integral algorithms are inherently more complicated and demanding than their GTO counterparts. In fact, we found that calculation of the STO integrals is one or two orders of magnitude more expensive than in the case of GTOs, with the same size of the basis set. This sounds daunting but the actual situation is more complex. For instance, in the largest basis sets used in this work, the calculation of the GTO two-electron integrals is a matter of several minutes, while in STOs it takes up to few hours. However, full CI or high-level CC calculations typically take several days to converge. Therefore, calculation of the integral files constitutes a small fraction of the total timing and does not pose any practical bottleneck. This is clearly a

TABLE X. Results of the selected theoretical predictions for the ground state of the beryllium dimer published since the late 1990s. All values are given in cm^{-1} and error bars are shown if estimated originally. Relativistic corrections are included if calculated. AE and FC denote all-electron and frozen-core, respectively. A majority of the acronyms appearing below is explained in the main text, apart from the following: ACPF, averaged coupled-pair functional; CC3, CC model with an approximate treatment of triple excitations; CAS, complete active space; MR-CISD+Q, MRCI with single and double excitations; Q denotes a specific Davidson-type correction for lack of size extensivity.

Year	Method	D_e	Reference
1999	FC CCSD(T)+FCI/CBS and AE CAS-ACPF	944 ± 25	Martin [33]
1999	CAS r_{12}-MR-ACPF/GTO($19s11p6d4f3g2h$)	898 ± 8	Gdanitz [34]
2000	CC3+FCI/d-aug-cc-pVQZ	885	Pecul *et al.* [35]
2005	EXRHF/GTO($23s10p8d6f3g2h$)	945 ± 15	Røggen and Veseth [31]
2007	AE CCSD(T)/CBS and FC FCI/CBS	938 ± 15	Patkowski *et al.* [32]
2007	Variational Monte Carlo and fixed-node diffusion Monte Carlo	829 ± 64	Harkless and Irikura [98]
2010	FC FCI/CBS and AE MR-CISD+Q	912	Schmidt *et al.* [27]
2010	AE MRCI/CBS	818	Mitin [28]
2011	AE CCSD(T)/CBS and FC FCI/CBS	935 ± 10	Koput [36]
2013	FC FCI/CBS and AE CCSD(T)/cc-pV6Z	927.4 ± 12	Evangelisti *et al.* [78]
2014	Density matrix renormalization group (DMRG)	931.2	Sharma *et al.* [37]
Present	FC FCI/CBS and AE CCSD(T)/MP4/CBS	929.0 ± 1.9	

consequence of relatively low scaling (N^4) of the calculations of the integral files, as compared with high-level CC of FCI methods.

It is also worth comparing our results with the latest theoretical values predicted by other authors. In Table X we collected most of the theoretical results published in the late 1990s and since then. An extensive bibliography of calculations published prior to this date can be found in Refs. [31] and [32]. Probably the most reliable calculations given thus far for the beryllium dimer are those of Patkowski *et al.* [32], giving 938 ± 15 cm^{-1}, and Koput [36], 935 ± 10 cm^{-1}. Our result is slightly lower but it lies within the error bars estimated by authors. Remarkably, the error predicted by us is by an order of magnitude smaller than in the previous works, despite that our estimations were rather conservative. Therefore, it seems that the theoretical values published thus far converge towards a value around 930 cm^{-1}, very close to the recent experimental result.

Apart from that, it is worth quoting three semiempirical results obtained by "morphing" the theoretical potential energy curve in order to reproduce the experimentally measured vibrational levels [44]. These values are 933.0, 933.2, and 934.6 cm^{-1}. It is difficult to estimate the error of these values but we feel that these semiempirical results are also consistent with our final value, 929.0 ± 1.9 cm^{-1}.

V. CONCLUSIONS AND OUTLOOK

We have obtained a reliable value of the interaction energy for the beryllium dimer by using STO basis sets combined with high-level quantum chemistry methods. The total error estimated by us, 1.9 cm^{-1}, is an order of magnitude smaller than in the previous theoretical works. The most striking advantages of STOs, as compared with GTOs, are the reliability in estimation of the core-core and core-valence correlation effects, very solid quality of extrapolations towards CBS, and improved performance in calculation of the one-electron relativistic effects. It is clear that all of these features are essential for a spectroscopically accurate determination of the potential energy curves for diatomic systems. We have not found a situation when STOs perform worse than GTO basis sets of the same size, at least among those available to us. Despite the fact that the evaluation of the two-electron integrals in the STO basis is much more computationally intensive than in the case of GTOs, we have never found it to be a practical bottleneck. An obvious disadvantage of STOs is the fact that two-electron, two-center integrals which are required for calculation of the Breit α^2 relativistic correction are very difficult to compute and we needed to resort to GTOs to compute them.

It is also worth considering the direction of further advancements which can be taken. Let us recall the fact that the ground state of the beryllium dimer is a very pathological and difficult system, e.g., the triple excitations are responsible for the bonding effects. In many different spectroscopically interesting diatomic systems the situation is not that difficult and the doubly excited determinants give the dominant contribution to the interaction energy. In such situations the explicitly correlated calculations [99,100] are an option, allowing for a much better saturation at the MP2, CCD, or CCSD levels of theory. The F12 theory of explicitly correlated calculations is now well established [101] but to apply STOs in such computations several issues of both technical and theoretical nature need to be resolved. For instance, for GTO calculations the exponential correlation factor of Ten-no [102,103] is nowadays routinely used. In the case of STO basis sets this choice is not feasible at present, due to an extremely complicated theory of evaluation of the resulting molecular two-electron integrals [104,105]. Therefore, a different correlation factor has to be adapted. Other problems such as quality and design of the auxiliary basis sets [106,107] for the resolution of identity approximation also need to be addressed. Nonetheless, the work on combining STO basis sets with explicitly correlated theories is in progress in our laboratory.

Let us suppose that the accuracy of calculation of the Born-Oppenheimer potential energy curves can be further improved by an order of magnitude, say, due to use of the explicitly correlated methods and other theoretical advancements. The dominant error would then come from inaccuracies in calculation of the relativistic effects, especially for heavier systems. If a perturbation theory, using the Breit-Pauli Hamiltonian, can be still applied then it is natural that two-electron relativistic effects should be calculated within the STO basis sets. Therefore, sooner or later we shall face the problem of evaluation of the matrix elements of the orbit-orbit and spin-orbit operators with the exponential functions. For heavy atoms, where the perturbation theory breaks down, different approaches need to be considered, such as Douglas-Kroll-Hess transformations [108–111] or use of effective core potentials [112,113]. Neither of the above methods can straightforwardly be combined with the STO basis sets. Nonetheless, our preliminary studies showed that extensions in these directions are feasible.

We can conclude by noting that the present series of papers opens up a possibility for a significant increase of accuracy which can be routinely reached for the diatomic systems with *ab initio* methods.

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