

Hylleraas-configuration-interaction analysis of the low-lying states in the three-electron Li atom and Be⁺ ion

María Belén Ruiz* and Johannes T. Margraf†

Department of Theoretical Chemistry, Friedrich-Alexander-University Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany

Alexei M. Frolov‡

Department of Applied Mathematics, University of Western Ontario, London, Ontario, Canada N6H 5B7

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The total energies of 28 bound *S*, *P*, *D*, *F*, *G*, *H*, and *I* states in the three-electron Li atom and Be⁺ ion, respectively, are determined with the use of the configuration interaction (CI) with Slater orbitals and *LS* eigenfunctions and the Hylleraas-configuration-interaction (Hy-CI) methods. We discuss the construction and selection of the configurations in the wave functions, optimization of the orbital exponents, and advanced computational techniques. Finally, we have developed an effective procedure which allows one to determine the energies of the excited states in three-electron atoms and ions to high accuracy by using compact wave functions. For the ground and low-lying excited states our best accuracy was $\approx 1 \times 10^{-6}$ a.u. with the Hy-CI method and 1×10^{-4} a.u. for other excited states. Analogous accuracy of the CI method is substantially lower, $\approx 1 \times 10^{-3}$ a.u. Rotationally excited (bound) states in the three-electron Li atom and Be⁺ ion are evaluated here to high accuracy.

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I. INTRODUCTION

Nowadays the Li atom has become, like the He atom years before, a system to test quantum chemistry and high-precision atomic physics [1]. The nonrelativistic wave functions of three-electron atoms and ions are of great interest in applications related to highly accurate evaluations of the lowest-order relativistic and QED corrections. At this moment we do not have any closed procedure which can be used to construct Dirac-type, manifestly Lorentz-invariant wave functions for two- and three-electron systems.

As a consequence, in actual applications such few-electron wave functions are approximated by the solutions of the nonrelativistic Schrödinger equation. All corrections are evaluated with the use of the regular Rayleigh-Schrödinger perturbation theory. Therefore, the nonrelativistic wave functions of three-electron atoms and ions are of paramount importance. On the other hand, the accuracy of modern laser-based atomic experiments allows one to determine many transition lines (or transition energies) in three-electron atoms and ions to an accuracy which could not be expected even 20 years ago. To match these experimental results we need to increase (and very substantially) the accuracy of our current nonrelativistic three-electron wave functions.

In the last few years the low-lying states of the Li atom have been calculated to the accuracy from a nanohartree to beyond a picohartree (1×10^{-9} – 10^{-12} a.u.) [2–6]. The corresponding wave functions usually contain many thousands of basis functions (or configurations). Such sets of basis functions used in these approaches include Hylleraas [7], Hylleraas-configuration-interaction [8] three-electron functions (and their close modifications). Recently, also the four-dimensional Gaussoid functions of the relative coordinates (see, e.g., [9,10]

and earlier references therein) has started to be used again for accurate calculations of the three-electron atomic systems. An alternative approach is based on the construction of the compact wave functions, which are constructed by selecting the most contributing basis functions (or configurations) and intensive optimization of the nonlinear parameters [11–15].

For the calculation of properties it would be desirable to have at hand all energies and wave functions for ground and all excited states. In addition, these states should be calculated with approximately the same accuracy. Moreover, numerous excited states of all symmetry types (*S*, *P*, *D*, *F*, *G*, *H*, *I*, ...) are usually needed, e.g., for the calculation of the probability of ionization. No less importantly, the computational time should be acceptable. The example of the Li atom can serve to test methods and techniques developed for the calculations of properties, such as excitation energies, transition probabilities, ionization energies, analysis of optical spectra, energy levels in confinement conditions, nuclear reactions and β^\pm decay, etc.; see, e.g., Ref. [16]

In this work we employ the Hylleraas-configuration-interaction (Hy-CI) method and the configuration interaction (CI) method with Slater orbitals and *LS* eigenfunctions to calculate a number of states of the Li atom and Be⁺ ion which lie below their respective energy limits of electronic ionization. The determination of non-*S* states with the Hy-CI wave function is easy, since the wave function retains the orbital picture. In the next sections we discuss the procedures for selecting the energetically important configurations and optimizing the orbital exponents in order to calculate accurate compact wave function expansions. Using this method we have obtained several benchmark energies.

II. THE Hy-CI AND CI METHODS

The Hy-CI method was proposed by Sims and Hagstrom [8,17,18]. The advantage of the Hy-CI method with respect to the other Hylleraas-type methods is that only up to one

*maria.belen.ruiz@fau.de

†johannes.margraf@fau.de

‡afrolov@uwo.ca

interelectronic coordinate r_{ij} per configuration is introduced into the wave function and, therefore, the method can, in principle, be applied to any atom. Calculations with the use of Hy-CI wave functions for few-electron atoms (from He to B) and for the H_2 molecule were reported in Refs. [2,19–24]. The CI wave function with Slater orbitals and LS eigenfunctions can be considered a basic part of the Hy-CI wave function. In this work we start our calculations with the CI wave functions. In this respect, we follow the same method as Weiss and Bunge [25,26] and use relatively small basis sets. Recent extensive CI calculations with Slater orbitals on Be and B atoms which are more accurate can be found in Refs. [27,28]. Both Hy-CI and CI wave functions can be summarized in the following expression:

$$\Psi = \sum_{p=1}^N C_p \Phi_p, \quad \Phi_p = \hat{O}(\hat{L}^2) \hat{A} \psi_p \chi. \quad (1)$$

The Hy-CI and CI wave functions are linear combinations of N symmetry-adapted configurations Φ_p and the coefficients C_p , which are determined variationally. In this work, the symmetry-adapted configurations are constructed “*a priori*” so that they are eigenfunctions of the angular momentum operator \hat{L}^2 . Another possibility would be the posterior projection of the configurations over the proper spatial space, as indicated in Eq. (1) by the projection operator $\hat{O}(\hat{L}^2)$, where \hat{A} is the antisymmetrization operator and χ is the spin eigenfunction.

In the case of the Li atom, it is sufficient to use only one spin function (formally a linear combination of the two possible spin eigenfunctions would be necessary):

$$\chi = [(\alpha\beta - \beta\alpha)\alpha]. \quad (2)$$

This is because the energetic contribution of the second spin eigenfunction has been proven to be small (in the order of

1×10^{-9} a.u. [3,29]). Moreover, the Slater determinants produced by the second spin eigenfunction ($2\alpha\alpha\beta - \beta\alpha\alpha - \alpha\beta\alpha$) (due to antisymmetry) are repeated when considering the first spin eigenfunction ($\alpha\beta\alpha - \beta\alpha\alpha$). The spatial part of the basis functions consists of Hartree products of Slater orbitals,

$$\psi_p = r_{ij}^\nu \prod_{k=1}^n \phi_k(r_k, \theta_k, \varphi_k), \quad (3)$$

where $\nu = 0, 1$ are employed for CI and Hy-CI wave functions, respectively. Powers $\nu > 1$ are effectively reduced to $\nu = 0, 1$, since all even and odd powers of r_{ij} can be expressed as a product of r_{ij} times a polynomial in r_i, r_j and angular functions.

The basis functions ϕ_p are products of Slater orbitals. For the CI wave functions presented in this work, we use $s, p, d, f, g, h,$ and i Slater orbitals. In contrast, for the Hy-CI wave functions we use only $s, p, d,$ and f Slater orbitals. Higher angular orbitals are, in practice, required only to obtain an accuracy in the nanohartree regime (1×10^{-9} a.u.) or higher with the Hy-CI method (see Ref. [2]). We use un-normalized complex Slater orbitals, for which the exponents are adjustable parameters. These are defined as

$$\phi(\mathbf{r}) = r^{n-1} e^{-\alpha r} Y_l^m(\theta, \varphi). \quad (4)$$

The spherical harmonics with Condon and Shortley phase [30, p. 52] are given by

$$Y_l^m(\theta, \varphi) = (-1)^m \left[\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!} \right]^{1/2} P_l^m(\cos \theta) e^{im\varphi}, \quad (5)$$

where $P_l^m(\cos \theta)$ are the associated Legendre functions. The spherical harmonics and associated Legendre functions used in this work are written explicitly in Ref. [31, p. 14].

The Hamiltonian in Hylleraas coordinates may be written in the infinite nuclear mass model [32,33]:

$$\begin{aligned} \hat{H} = & -\frac{1}{2} \sum_{i=1}^n \frac{\partial^2}{\partial r_i^2} - \sum_{i=1}^n \frac{1}{r_i} \frac{\partial}{\partial r_i} - \sum_{i=1}^n \frac{Z}{r_i} - \sum_{i<j}^n \frac{\partial^2}{\partial r_{ij}^2} - \sum_{i<j}^n \frac{2}{r_{ij}} \frac{\partial}{\partial r_{ij}} + \sum_{i<j}^n \frac{1}{r_{ij}} - \frac{1}{2} \sum_{i \neq j}^n \frac{r_i^2 + r_j^2 - r_{ij}^2}{r_i r_{ij}} \frac{\partial^2}{\partial r_i \partial r_{ij}} \\ & - \frac{1}{2} \sum_{i \neq j}^n \sum_{k>j}^n \frac{r_{ij}^2 + r_{ik}^2 - r_{jk}^2}{r_{ij} r_{ik}} \frac{\partial^2}{\partial r_{ij} \partial r_{ik}} - \frac{1}{2} \sum_{i=1}^n \frac{1}{r_i^2} \frac{\partial^2}{\partial \theta_i^2} - \frac{1}{2} \sum_{i=1}^n \frac{1}{r_i^2 \sin^2 \theta_i} \frac{\partial^2}{\partial \varphi_i^2} - \frac{1}{2} \sum_{i=1}^n \frac{\cot \theta_i}{r_i^2} \frac{\partial}{\partial \theta_i} \\ & - \sum_{i \neq j}^n \left(\frac{r_j}{r_i r_{ij}} \frac{\cos \theta_j}{\sin \theta_i} + \frac{1}{2} \cot \theta_i \frac{r_{ij}^2 - r_i^2 - r_j^2}{r_i^2 r_{ij}} \right) \frac{\partial^2}{\partial \theta_i \partial r_{ij}} - \sum_{i \neq j}^n \frac{r_j}{r_i r_{ij}} \frac{\sin \theta_j}{\sin \theta_i} \sin(\varphi_i - \varphi_j) \frac{\partial^2}{\partial \varphi_i \partial r_{ij}}. \end{aligned} \quad (6)$$

The angular momentum operator can be extracted from Eq. (6),

$$\begin{aligned} \sum_{i=1}^n \frac{1}{r_i^2} \hat{L}_i^2 = & -\frac{1}{2} \sum_{i=1}^n \frac{1}{r_i^2} \frac{\partial^2}{\partial \theta_i^2} - \frac{1}{2} \sum_{i=1}^n \frac{1}{r_i^2 \sin^2 \theta_i} \frac{\partial^2}{\partial \varphi_i^2} \\ & - \frac{1}{2} \sum_{i=1}^n \frac{\cot \theta_i}{r_i^2} \frac{\partial}{\partial \theta_i}, \end{aligned} \quad (7)$$

and its eigenvalue equation is

$$L_i^2 \phi_i = l_i(l_i + 1) \phi_i, \quad (8)$$

with l_i being the angular momentum quantum number of the orbital ϕ_i . In the case of Hy-CI wave functions, the variables $\partial^2/(\partial r_{ij} \partial r_{ik})$ vanish.

The kinetic energy operator has been separated into several radial and angular parts. This operator has the advantage that, for the case of three-electron kinetic integrals, the expansion of r_{ij} into $r_<$ and $r_>$ is avoided, and therefore no three-electron auxiliary integrals W are required; see Ref. [34]. This fact saves not only calculations, but also memory space. Only the easily computed two-electron auxiliary integrals $V(n, m; \alpha, \beta)$ are needed.

From the variational principle, one obtains the matrix eigenvalue problem

$$(\mathbf{H} - E\mathbf{S})\mathbf{C} = \mathbf{0}, \quad (9)$$

where the matrix elements are

$$H_{kl} = \int \Phi_k H \Phi_l d\tau, \quad S_{kl} = \int \Phi_k \Phi_l d\tau. \quad (10)$$

The integrals occurring in the Hy-CI calculations of three-electron systems, can be divided into two- and three-electron integrals. The two-electron integrals are of the types

$$\begin{aligned} \langle r_{12} \rangle, \quad \langle r_{12}^2 \rangle, \quad \left\langle \frac{1}{r_{12}} \right\rangle, \\ \langle r_{12} \rangle \langle r_{34} \rangle, \quad \langle r_{12} \rangle \left\langle \frac{1}{r_{34}} \right\rangle, \end{aligned} \quad (11)$$

where the notation $\langle r_{12} \rangle$ represents an integral, in which orbitals of electrons 1 and 2 are involved on the left- and right-hand sides, e.g.,

$$\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)r_{12}\phi(\mathbf{r}_1)\phi(\mathbf{r}_2) \rangle. \quad (12)$$

These two-electron integrals were evaluated with the algorithms described in Ref. [35].

The three-electron integrals are of the following types:

$$\langle r_{12}r_{13} \rangle, \quad \langle r_{12}^2r_{13} \rangle, \quad \left\langle \frac{r_{12}}{r_{13}} \right\rangle, \quad \left\langle \frac{r_{12}r_{13}}{r_{23}} \right\rangle. \quad (13)$$

The first three cases are evaluated by direct integration over one r_{ij} and the coordinates of one electron. They are thus reduced to a linear combination of two-electron integrals [36]. For the so-called triangle integrals $\langle r_{12}r_{13}/r_{23} \rangle$ we use a very efficient subroutine by Sims and Hagstrom [37]. Finally the two- and three-electron kinetic energy integrals are evaluated using the Hamiltonian of Eq. (6) [34,35].

The integration of these three-electron integrals leads to a limited linear combination of two-electron integrals. These can be calculated very accurately in terms of two-electron auxiliary integrals $V(m, n; \alpha, \beta)$, defined as

$$V(m, n; \alpha, \beta) = \int_0^\infty r_1^m e^{-\alpha r_1} dr_1 \int_{r_1}^\infty r_2^n e^{-\beta r_2} dr_2. \quad (14)$$

The two-electron auxiliary integrals with positive indices m, n are, in turn, evaluated in terms of one-electron auxiliary integrals $A(n, \alpha)$ [38].

In summary, only two-electron integrals, as in the CI method, and triangle integrals have to be computed. This fact will be extremely helpful when extending the application of the Hy-CI method to larger systems. In our code, approximately the same amount of memory is required for CI and Hy-CI calculations. Note also that, if the Hy-CI method is applied to many-electron atoms or molecules, the highest order of required electron integrals is four.

To perform these computations, we have written a three-electron Hy-CI computer program for three-electron systems in Fortran 90. The calculations were conducted with the use of quadruple precision arithmetics. The program has been thoroughly checked by comparing results of our numerical calculations with the results by Sims and Hagstrom [2] and

King [12] for the lithium atom. In these calculations we have obtained complete agreement.

III. CALCULATIONS

A. Construction and selection of the symmetry-adapted configurations

The ground-state configuration of the Li atom and Be^+ ion is *sss* [i.e., $s(1)s(2)s(3)$]. The further considered configurations for *S* symmetry states ($L = 0$) are, ordered by decreasing energetic contribution, *spp*, *pps*, *sdd*, *dds*, *sff*, and *ffs*. The energetically important configurations for $L = 0-6$ are listed in Table I. The quantum number $M = 0$ was chosen because for this case a smaller number of Slater determinants is required. We performed a systematical selection of the CI configurations according to their energy contribution. This was done by performing calculations on blocks constructed for all possible configurations. The eigenvalue equation was diagonalized upon each addition of a configuration. In this manner, the contribution of every single configuration and of each block of a given type to the total energy was evaluated. Configurations with an overall energy contribution below 1×10^{-8} a.u. were not considered.

Usually the contribution of a configuration is larger, the smaller is the sum of the l quantum numbers of the employed orbitals $l_1 + l_2 + l_3$; i.e., the contribution of the configuration *spp* > *ppp* for a *P* state. In cases such as the *P* states *spd* and *ppp*, where the sum of l_i is equal, the two inner electrons in *ppp* form a *S* configuration. The resulting three-electron configuration is $(^1S)p$ (a *P* configuration) and contributes more than the *spd* one. This is especially important in the case of *F*, *G*, *H*, and *I* states. Among the many possibilities to construct configurations of these symmetries, the energetically most important configurations were proven to be those with an inner *S* shell and a single occupied orbital with the symmetry of the state under consideration, i.e., $(^1S)f$, $(^1S)g$, $(^1S)h$, and $(^1S)i$. The inner shell is described with a sum of configurations $(^1S) = ss + pp + dd + ff + gg + hh + ii$. In the CI calculations of *S*, *P*, and *D* states we employed *s*, *p*, *d*, and *f* orbitals (see Table I). In the CI calculations of the *F*, *G*, *H*, and *I* states we have used in addition *g*, *h*, and *i* orbitals as shown in Table I. The energetic order determined for the CI calculations was kept for the Hy-CI calculations, where every CI configuration is multiplied by an interelectronic distance: $\text{Hy-CI} = \text{CI} \times \{1 + r_{12} + r_{13} + r_{23}\}$.

Obviously, more types of configurations than the ones discussed here can be constructed for a given L quantum number. For instance, configurations like *psp* could be considered, if the exponents $\alpha_1 \neq \alpha_2$. However, we kept the orbital exponents in the *K* shell equal; see Tables II and III. Therefore, the configuration *psp* is equivalent to the configuration *spp*. Other possible higher energy configurations like *ppp* for $L = 0$, $M = 0$ exist, but were discarded due to their energetic contribution. Table I shows how the configurations used in this work were constructed from *s*, *p*, *d*, *f*, *g*, *h*, and *i* Slater orbitals.

Finally, there are more possible “degenerate L eigenfunction” solutions with a larger number of Slater determinants. Specifically, these are degenerate with respect to the quantum numbers L and M , but with possible different

TABLE I. List of the symmetry-adapted configurations with quantum numbers $L = 0-6$ and $M_Z = 0$ employed in the CI and Hy-CI calculations of the Li atom and Be^+ ion. The notation sss stands for $s(1)s(2)s(3)$. The Hy-CI configurations are obtained from the CI ones by multiplying them by the factor $R = \{1 + r_{12} + r_{13} + r_{23}\}$. Normalization factors are omitted.

L	Configurations	Construction
0	sss	sss
0	spp	$sp_0p_0 - sp_1p_{-1} - sp_{-1}p_1$
0	pps	$p_0p_0s - p_1p_{-1}s - p_{-1}p_1s$
0	sdd	$sd_0d_0 - sd_1d_{-1} - sd_{-1}d_1 + sd_2d_{-2} + sd_{-2}d_2$
0	dds	$d_0d_0s - d_1d_{-1}s - d_{-1}d_1s + d_2d_{-2}s + d_{-2}d_2s$
0	sff	$sf_0f_0 - sf_1f_{-1} - sf_{-1}f_1 + sf_2f_{-2} + sf_{-2}f_2 - sf_3f_{-3} - sf_{-3}f_3$
0	ffs	$f_0f_0s - f_1f_{-1}s - f_{-1}f_1s + f_2f_{-2}s + f_{-2}f_2s - f_3f_{-3}s - f_{-3}f_3s$
1	ssp	ssp_0
1	sps	sp_0s
1	ppp	$p_0p_0p_0 - p_1p_{-1}p_0 - p_{-1}p_1p_0$
1	ddp	$d_0d_0p_0 - d_1d_{-1}p_0 - d_{-1}d_1p_0 + d_2d_{-2}p_0 + d_{-2}d_2p_0$
1	pdd	$p_0d_0d_0 - p_0d_1d_{-1} - p_0d_{-1}d_1 + p_0d_2d_{-2} + p_0d_{-2}d_2$
1	spd	$sp_0d_0 - sp_1d_{-1} - sp_{-1}d_1$
1	pds	$p_0d_0s - p_1d_{-1}s - p_{-1}d_1s$
1	sdp	$sd_0p_0 - sd_1p_{-1} - sd_{-1}p_1$
2	ssd	ssd_0
2	sds	sd_0s
2	spp	$sp_0p_0 + sp_1p_{-1} + sp_{-1}p_1$
2	pps	$p_0p_0s + p_1p_{-1}s + p_{-1}p_1s$
2	ppd	$p_0p_0d_0 - p_1p_{-1}d_0 - p_{-1}p_1d_0$
2	ddd	$d_0d_0d_0 - d_1d_{-1}d_0 - d_{-1}d_1d_0 + d_2d_{-2}d_0 + d_{-2}d_2d_0$
2	spf	$sp_0f_0 - sp_1f_{-1} - sp_{-1}f_1$
2	pfs	$p_0f_0s - p_1f_{-1}s - p_{-1}f_1s$
2	sfp	$sf_0p_0 - sf_1p_{-1} - sf_{-1}p_1$
3	ssf	ssf_0
3	sfs	sf_0s
3	ppf	$p_0p_0f_0 - p_1p_{-1}f_0 - p_{-1}p_1f_0$
3	ddf	$d_0d_0f_0 - d_1d_{-1}f_0 - d_{-1}d_1f_0 + d_2d_{-2}f_0 + d_{-2}d_2f_0$
3	fff	$f_0f_0f_0 - f_1f_{-1}f_0 - f_{-1}f_1f_0 + f_2f_{-2}f_0 + f_{-2}f_2f_0 - f_3f_{-3}f_0 - f_{-3}f_3f_0$
3	ggf	$g_0g_0f_0 - g_1g_{-1}f_0 - g_{-1}g_1f_0 + g_2g_{-2}f_0 + g_{-2}g_2f_0 - g_3g_{-3}f_0 - g_{-3}g_3f_0 + g_4g_{-4}f_0 + g_{-4}g_4f_0$
3	hhf	$h_0h_0f_0 - h_1h_{-1}f_0 - h_{-1}h_1f_0 + h_2h_{-2}f_0 + h_{-2}h_2f_0 - h_3h_{-3}f_0 - h_{-3}h_3f_0 + h_4h_{-4}f_0 + h_{-4}h_4f_0 - h_5h_{-5}f_0 - h_{-5}h_5f_0$
4	ssg	ssg_0
4	sgs	sg_0s
4	ppg	$p_0p_0g_0 - p_1p_{-1}g_0 - p_{-1}p_1g_0$
4	ddg	$d_0d_0g_0 - d_1d_{-1}g_0 - d_{-1}d_1g_0 + d_2d_{-2}g_0 + d_{-2}d_2g_0$
4	ffg	$f_0f_0g_0 - f_1f_{-1}g_0 - f_{-1}f_1g_0 + f_2f_{-2}g_0 + f_{-2}f_2g_0 - f_3f_{-3}g_0 - f_{-3}f_3g_0$
4	ggg	$g_0g_0g_0 - g_1g_{-1}g_0 - g_{-1}g_1g_0 + g_2g_{-2}g_0 + g_{-2}g_2g_0 - g_3g_{-3}g_0 - g_{-3}g_3g_0 + g_4g_{-4}g_0 + g_{-4}g_4g_0$
4	hhg	$h_0h_0g_0 - h_1h_{-1}g_0 - h_{-1}h_1g_0 + h_2h_{-2}g_0 + h_{-2}h_2g_0 - h_3h_{-3}g_0 - h_{-3}h_3g_0 + h_4h_{-4}g_0 + h_{-4}h_4g_0 - h_5h_{-5}g_0 - h_{-5}h_5g_0$
5	ssh	ssh_0
5	shs	sh_0s
5	pph	$p_0p_0h_0 - p_1p_{-1}h_0 - p_{-1}p_1h_0$
5	ddh	$d_0d_0h_0 - d_1d_{-1}h_0 - d_{-1}d_1h_0 + d_2d_{-2}h_0 + d_{-2}d_2h_0$
5	ffh	$f_0f_0h_0 - f_1f_{-1}h_0 - f_{-1}f_1h_0 + f_2f_{-2}h_0 + f_{-2}f_2h_0 - f_3f_{-3}h_0 - f_{-3}f_3h_0$
5	ggh	$g_0g_0h_0 - g_1g_{-1}h_0 - g_{-1}g_1h_0 + g_2g_{-2}h_0 + g_{-2}g_2h_0 - g_3g_{-3}h_0 - g_{-3}g_3h_0 + g_4g_{-4}h_0 + g_{-4}g_4h_0$
5	hhh	$h_0h_0h_0 - h_1h_{-1}h_0 - h_{-1}h_1h_0 + h_2h_{-2}h_0 + h_{-2}h_2h_0 - h_3h_{-3}h_0 - h_{-3}h_3h_0 + h_4h_{-4}h_0 + h_{-4}h_4h_0 - h_5h_{-5}h_0 - h_{-5}h_5h_0$
6	ssi	ssi_0
6	sis	si_0s
6	ppi	$p_0p_0i_0 - p_1p_{-1}i_0 - p_{-1}p_1i_0$
6	ddi	$d_0d_0i_0 - d_1d_{-1}i_0 - d_{-1}d_1i_0 + d_2d_{-2}i_0 + d_{-2}d_2i_0$
6	ffi	$f_0f_0i_0 - f_1f_{-1}i_0 - f_{-1}f_1i_0 + f_2f_{-2}i_0 + f_{-2}f_2i_0 - f_3f_{-3}i_0 - f_{-3}f_3i_0$
6	ggi	$g_0g_0i_0 - g_1g_{-1}i_0 - g_{-1}g_1i_0 + g_2g_{-2}i_0 + g_{-2}g_2i_0 - g_3g_{-3}i_0 - g_{-3}g_3i_0 + g_4g_{-4}i_0 + g_{-4}g_4i_0$

TABLE I. (Continued.)

L	Configurations	Construction
6	hhi	$h_0h_0i_0 - h_1h_{-1}i_0 - h_{-1}h_1i_0 + h_2h_{-2}i_0 + h_{-2}h_2i_0 - h_3h_{-3}i_0 - h_{-3}h_3i_0 + h_4h_{-4}i_0$ $+ h_{-4}h_4i_0 - h_5h_{-5}i_0 - h_{-5}h_5i_0$
6	iii	$i_0i_0i_0 - i_1i_{-1}i_0 - i_{-1}i_1i_0 + i_2i_{-2}i_0 + i_{-2}i_2i_0 - i_3i_{-3}i_0 - i_{-3}i_3i_0 + i_4i_{-4}i_0 + i_{-4}i_4i_0 - i_5i_{-5}i_0$ $- i_{-5}i_5i_0 + i_6i_{-6}i_0 + i_{-6}i_6i_0$

energy contribution, i.e., nondegenerate with respect to the energy [26]. Although the inclusion of various degenerate configurations has been shown to improve the energy of the state, this contribution is very small. This is important for very accurate CI calculations, as reported, e.g., by Bunge [27,28]. In our work, we have concentrated on the energetically most important CI configurations in order to use them as the basis for Hy-CI configurations (i.e., configurations multiplied by an interelectronic distance r_{ij}).

After selecting the types of configurations, we constructed complete blocks of these configurations for a given basis set. For instance, for the basis $n = 4$ (i.e., $[4s3p2d1f]$ or $[1s2s3s4s2p3p3d4f]$) in the sss block the following configurations were considered: $1s1s2s$, $1s2s2s$, $2s2s2s$, $1s1s3s$, $1s2s3s$, $2s2s3s$, \dots , $4s4s4s$. Note that the configuration $1s1s1s$ has no physical meaning but displays a large

energy contribution. Altogether, our CI calculations can be considered “selected” with respect to the type of configuration, and “full-CI” with respect to the orbitals basis set.

Another important aspect in CI and Hy-CI calculations is the symmetry adaptation of the configurations. As mentioned above, the configurations are constructed *a priori* to be eigenfunctions of the angular momentum operator \hat{L}^2 . In the sums of Table I, the configurations are formed by Slater determinants. The determinants are pairwise symmetric (i.e., sp_1p_{-1} and $sp_{-1}p_1$ in the spp configuration) and lead to the same values of the electronic integrals. Therefore, it is possible and desirable to consider only one of the determinants and to deduce the result from the other.

In other words, the solution of the eigenvalue problem obtained when using reduced 1×1 matrix elements (where the integrals are added, configuration $sp_1p_{-1} + sp_{-1}p_1$) or when

TABLE II. Orbital exponents used in the CI and Hy-CI calculations of the Li atom of Tables IV and VI. The shells are doubly occupied $\alpha = \beta$ and γ is the exponent of the single occupied orbital. The virial factor has been obtained during the optimization of orbital exponents.

No.	State	$\alpha_{CI} = \beta_{CI}$	γ_{CI}	Virial _{CI}	$\alpha_{Hy-CI} = \beta_{Hy-CI}$	γ_{Hy-CI}	Virial _{Hy-CI}
1	2^2S	4.644 060	1.107 868	2.000 000	2.994 250	0.839 625	2.000 000
3	3^2S	4.698 079	0.561 144	2.000 000	3.550 050	0.438 800	2.000 028
6	4^2S	4.605 560	0.359 164	2.000 196	3.241 342	0.304 425	2.000 483
10	5^2S	4.639 431	0.258 794	2.001 368	3.906 990	0.235 023	2.000 534
15	6^2S	4.602 371	0.191 464	2.003 141	4.602 371	0.191 464	2.002 362
24	7^2S	4.696 442	0.154 444	2.002 970	3.384 262	0.134 132	2.003 046
28	8^2S	5.039 868	0.094 174	2.003 949	2.857 940	0.134 896	2.003 993
2	2^2P	4.451 592	0.827 973	2.000 016	3.140 842	0.725 092	2.000 000
4	3^2P	4.507 292	0.504 441	2.000 053	3.520 217	0.370 508	2.000 087
7	4^2P	4.486 842	0.320 982	2.000 175	3.523 842	0.255 675	2.001 194
13	5^2P	4.577 346	0.230 959	2.000 776	3.844 842	0.204 309	2.001 203
19	6^2P	4.513 159	0.169 635	2.003 267	3.426 592	0.170 633	2.001 447
26	7^2P	4.581 002	0.144 740	2.004 915	3.971 050	0.144 667	2.003 926
5	3^2D	4.512 037	0.459 812	2.000 000	3.359 717	0.347 508	2.000 005
8	4^2D	4.483 217	0.247 508	2.000 012	3.496 259	0.253 341	1.999 654
14	5^2D	4.483 288	0.200 160	2.000 073	3.841 288	0.200 160	2.000 234
20	6^2D	4.539 008	0.166 704	2.000 433	4.960 208	0.150 343	2.003 830
27	7^2D	4.492 642	0.143 125	2.001 133	4.492 642	0.143 125	2.000 086
9	4^2F	4.630 029	0.299 372	2.000 027			
12	5^2F	4.645 336	0.186 989	2.000 041			
18	6^2F	4.669 615	0.174 730	2.000 061			
25	7^2F	4.763 930	0.141 984	2.000 367			
11	5^2G	5.165 095	0.234 090	1.999 983			
17	6^2G	5.127 263	0.207 967	1.999 997			
26	7^2G	5.076 262	0.142 897	2.000 050			
16	6^2H	5.077 561	0.181 168	2.000 011			
22	7^2H	5.077 536	0.141 189	2.000 021			
21	7^2I	5.077 551	0.144 224	2.000 014			

TABLE III. Orbital exponents used in the CI and Hy-CI calculations of the Be^+ ion of Tables V and VII. The shells are doubly occupied $\alpha = \beta$ and γ is the exponent of the single occupied orbital. The virial factor has been obtained during the optimization of orbital exponents.

No.	State	$\alpha_{\text{CI}} = \beta_{\text{CI}}$	γ_{CI}	Virial _{CI}	$\alpha_{\text{Hy-CI}} = \beta_{\text{Hy-CI}}$	$\gamma_{\text{Hy-CI}}$	Virial _{Hy-CI}
1	2^2S	6.345 407	1.950 188	2.000 000	4.173 235	1.406 372	2.000 000
3	3^2S	6.307 744	1.019 290	2.000 017	4.838 717	0.876 476	2.000 009
6	4^2S	6.280 890	0.665 840	2.000 087	4.766 466	0.585 863	2.000 153
10	5^2S	6.327 154	0.479 516	2.001 115	5.331 658	0.442 445	2.001 495
15	6^2S	6.304 912	0.364 545	2.003 618	5.150 658	0.401 445	2.000 714
21	7^2S	6.341 861	0.304 815	2.004 436	4.475 332	0.287 333	2.002 761
28	8^2S	6.397 917	0.248 083	2.005 359	4.201 068	0.260 587	2.003 766
2	2^2P	6.141 069	1.760 345	2.000 000	4.746 625	1.321 000	2.000 002
4	3^2P	6.148 030	0.964 810	2.000 031	4.837 058	0.712 777	2.000 045
7	4^2P	6.158 844	0.631 221	2.000 183	4.800 125	0.516 000	2.000 749
11	5^2P	6.168 223	0.465 315	2.001 420	5.069 200	0.532 429	2.000 760
19	6^2P	6.189 834	0.344 862	2.006 738	3.951 567	0.339 598	2.007 193
26	7^2P	6.222 913	0.290 957	2.010 724	4.743 317	0.289 533	2.008 245
5	3^2D	6.132 817	0.867 614	2.000 005	4.804 284	0.670 348	2.000 004
9	4^2D	6.159 980	0.591 028	2.000 005	4.750 784	0.588 652	2.000 012
14	5^2D	6.134 907	0.434 209	2.000 047	5.720 102	0.381 441	2.000 363
20	6^2D	6.484 197	0.337 802	2.000 781	5.539 008	0.443 304	2.000 114
27	7^2D	6.157 877	0.286 801	2.002 368	4.849 877	0.286 801	2.001 541
8	4^2F	6.440 871	0.589 239	1.999 989			
13	5^2F	6.446 382	0.372 527	2.000 019			
18	6^2F	6.352 375	0.344 411	2.000 119			
25	7^2F	6.419 948	0.285 310	2.000 794			
12	5^2G	6.844 762	0.442 011	2.000 017			
17	6^2G	6.896 092	0.360 327	2.000 012			
24	7^2G	7.030 220	0.289 953	2.000 041			
16	6^2H	6.923 097	0.337 191	2.000 007			
23	7^2H	6.902 410	0.283 624	2.000 024			
22	7^2I	6.977 235	0.288 487	2.000 000			

using explicit 2×2 matrix elements of the Slater determinants is the same. The symmetry adaptation is computationally favorable, since the number of Slater determinants in the input is smaller and the repeated computation of equal integrals is avoided. As can be seen in Table I, this procedure may be applied to all the constructed configurations.

The Hy-CI configuration blocks were constructed by including (1) the corresponding CI block, (2) the CI block multiplied by the interelectronic coordinate r_{12} , (3) the CI block multiplied by r_{13} , and (4) the CI block multiplied by r_{23} . Here, one has to take into account possible symmetries between equivalent configurations. This can produce linear dependencies which cause the calculation to break down (due to linearly dependent equations in the eigenvalue problem). For example, $2s2s3s \cdot r_{13}$ is equal or equivalent to $2s2s3s \cdot r_{23}$.

In general, energetically important Hy-CI configurations must not be the same as the corresponding CI ones, but usually this is the case. Therefore, we constructed Hy-CI blocks of configurations based on the selected CI ones. The number of configurations grows very fast when adding the three r_{ij} factors. Therefore, we filtered the configurations within a block one by one, calculating the total energy E_i every time a single configuration was added and comparing it to the total energy without this configuration E_{i-1} .

Again, if the difference of the energy was smaller than the energy criterion $|E_{i-1} - E_i| < 1 \times 10^{-8}$ a.u., the new configuration was discarded. In this manner, all configurations were checked, leading to a relatively compact Hy-CI wave function. Since the configuration selection process was carried out for every state, the length of the final wave functions and the configurations included differ from state to state and between Li and Be^+ . This is natural, since we need different configurations to describe different excited states.

B. Optimization of the orbital exponents

The orbital exponents were optimized for each atomic state of the Li atom and Be^+ ion. A set of two exponents was used (one for the K shell and the other for the odd-electron in the L shell) and kept equal for all configurations. This technique accelerates the computations, while still producing sufficiently accurate results for the calculation of properties. It is clear that, for highly accurate energies beyond microhartree accuracy (1×10^{-6} a.u.), more flexibility in the exponents is needed, as shown in recent calculations on the lithium atom with extensive optimization [2,12–14] or in calculations with very large wave functions and carefully chosen exponents [2,3,6,29].

The virial factor,

$$\chi = -\frac{\langle V \rangle}{\langle T \rangle}, \quad (15)$$

is used to check the quality of the wave function and guides the numerical optimization of the exponents in the trial wave functions. In general, it is observed that the accuracy obtained in the virial factor predicts approximately the number of the accurate decimal digits in the energy. For instance, the ground-state energy of the Li atom has been calculated to $-7.478\,058\,893$ a.u. (six decimal digits accurate) and its corresponding virial factor is $2.000\,000\,954$ (six digits are zero), whereas the higher energy state 6^2S with energy $-7.295\,739\,603$ a.u. (three decimal digits accurate) has a virial factor of $2.002\,361$.

The optimization of two exponents at the same time, in the case of Li for all configurations, has the advantage that (being a global optimization) it is very fast, in contrast with the partial optimization of configurations one by one, which may take very long computational times.

The optimization of the orbital exponents was carried out via a parabolic procedure. Shortly, the orbital exponents are

varied by a step size. Three energy values are thus calculated and fitted to a parabola, and the minimum of the parabola is calculated. Subsequently, this value is kept fixed and the same is done for the next exponent. The step size is continually decreased by a given factor as the cycles of exponent optimization are repeated. At every step the virial factor is calculated. The optimization is performed until the energy no longer improves, and the best virial and energy values agree. The optimization program is completely automatic and the exponents can be optimized for every state and nuclear charge.

For the CI calculations, the orbital exponents were optimized until the same energy minimum was obtained in two successive optimizations, starting with a basis of $n = 4$. These exponents were then used in a CI calculation with the basis $n = 5$ and optimized again, and so on, up to the basis $n = 7$. The optimized exponents of the basis $n = 7$ are reported in Table II. For Be^+ the same procedure was repeated with the nuclear charge $Z = 4$. The excited states were determined by optimization of the orbital exponents for the second, third, ... eigenvalue. Note that in strictly variational methods,

TABLE IV. Convergence of Full-CI (LS) calculations on the ground and excited states of the Li atom with respect to the basis set. The basis sets are constructed with Slater orbitals; see Table I. The optimized orbital exponents for the largest basis are given in Table II. No. is the ordering number of the state. N is the number of symmetry-adapted configurations (Table I). All energies are given in a.u., while Difference refers to the energy differences between the present and the reference energies in microhartrees (1×10^{-6} a.u.).

No.	State	N	$n = 6$	N	$n = 7$	N	Reference energy	Ref.	Difference
1	2^2S	596	-7.476 817	991	-7.477 192	34020	-7.478 060 323 910 146 894	[3]	868.7
3	3^2S	596	-7.352 980	991	-7.353 249	34020	-7.354 098 421 444 364 045	[3]	849.7
6	4^2S	596	-7.317 410	991	-7.317 679	34020	-7.318 530 845 998 906 901	[3]	851.9
10	5^2S	596	-7.302 342	991	-7.302 682	34020	-7.303 551 579 226 734 650	[3]	870.0
15	6^2S	596	-7.294 676	991	-7.294 935	34020	-7.295 859 510 844 131 039	[3]	924.3
24	7^2S			991	-7.289 596	17072	-7.291 392 273 116	[2]	1796.3
					$n = 8^a$				
28	8^2S			508	-7.285 695				
2	2^2P	849	-7.408 437	1430	-7.408 619	32200	-7.410 156 532 652 370	[3]	1537.8
4	3^2P	849	-7.335 436	1430	-7.335 658	7000	-7.337 151 707 93	[4]	1493.5
7	4^2P	849	-7.310 200	1430	-7.310 383	7000	-7.311 889 059 38	[4]	1506.1
13	5^2P	849	-7.298 615	1430	-7.298 802	7000	-7.300 288 164 88	[4]	1486.0
19	6^2P	849	-7.292 380	1430	-7.292 545	7000	-7.294 020 052 93	[4]	1475.3
26	7^2P			1430	-7.288 749	7000	-7.290 254 908 09	[4]	1506.0
5	3^2D	646	-7.333 935	1056	-7.334 100	32760	-7.335 523 543 524 685	[3]	1423.5
8	4^2D	646	-7.309 598	1056	-7.309 761	4000	-7.311 189 578 43	[5]	1428.1
14	5^2D	646	-7.298 340	1056	-7.298 502	4000	-7.299 927 555 94	[5]	1425.6
20	6^2D	646	-7.292 225	1056	-7.292 387	4000	-7.293 810 713 64	[5]	1423.5
27	7^2D			1056	-7.288 700	4000	-7.290 122 856 24	[5]	1422.2
9	4^2F	286	-7.310 288	532	-7.310 610		-7.311 168 7	[12]	559.1
12	5^2F	286	-7.298 989	532	-7.299 340		-7.299 917 1	[12]	576.8
18	6^2F	286	-7.292 769	532	-7.293 211				
25	7^2F			532	-7.289 401				
			$n = 7$		$n = 8$				
11	5^2G	395	-7.299 248	694	-7.299 430				
17	6^2G	395	-7.293 125	694	-7.293 294				
26	7^2G	395	-7.289 383	694	-7.289 605				
16	6^2H	272	-7.293 138	519	-7.293 320				
22	7^2H	272	-7.289 435	519	-7.289 625				
21	7^2I			350	-7.289 638				

^aFor the calculation of the 8^2S , 7^2G , 7^2H , and 7^2I states larger basis sets including $n = 8$ orbitals are needed.

the successive excited states are the roots of the eigenvalue problem. The exponent γ of the singly occupied orbital gets smaller as the quantum number increases. We have obtained energies that are about 1 millihartree accurate (1×10^{-3} a.u.) with respect to the nonrelativistic values reported in the literature.

The Hy-CI orbital exponents of the three lower states of every symmetry were optimized using a basis set $n = 4$ of about 400 configurations of all types considered. Subsequently, the exponents were kept fixed for calculations with $n = 5-8$ basis sets. The orbital exponents for the higher excited states were optimized using few types of configurations (the energetically most important ones) and a larger basis set $n = 8$. In Tables II and III the optimized exponents of the CI and Hy-CI wave functions are given. Note that the CI exponents are in general larger than the Hy-CI ones. This is in part because the Hy-CI wave functions employ a smaller basis set.

The described method of optimization of the exponents is very successful for the determination of ground and low-lying excited states. For higher excited states, is not possible to obtain a good virial factor with this type of optimization. A larger orbital basis and more flexibility in the number of exponents would be needed.

IV. RESULTS

We calculated S , P , D , F , G , H , and I symmetry states for the Li atom with the CI method, using the symmetry-adapted configurations shown in Table I. The CI calculations were carried out using double precision arithmetic (about 15 decimal digits accuracy on our workstations). In this manner, we determined the energy of seven S states, six P states, five D states, four F states, three G states, two H states, and one I state.

The total energies of the 28 states of the Li atom considered in this study are below the total energy of the ground state of the ${}^{\infty}\text{Li}^+$ ion, i.e., $E_{\text{tr}} \approx -7.279\,913\,412\,669\,305\,964\,918\,75(25)$ a.u. [39]. This total energy of the ground state in the two-electron ${}^{\infty}\text{Li}^+$ ion is the natural threshold energy for an arbitrary bound state in the three-electron Li atom.

For the Be^+ ion we determined the total energies of the 28 bound states, including seven S states, six P states, five D states, four F states, three G states, two H states, and one I state. The results of our calculations can be found in Tables IV and V. In all these calculations we applied the CI method. The computed energies are lower than the corresponding ionization energy of the Be^+ ion [20]. The accuracy of the

TABLE V. Convergence of Full-CI (LS) calculations on the ground and excited states of the Be^+ ion with respect to the basis set. The basis set and symmetry-adapted configurations used are the same than for the Li atom calculations of Table IV. All energies are given in a.u., while Difference refers to the energy differences between the present and the reference energies in microhartrees (1×10^{-6} a.u.).

No.	State	N	$n = 6$	N	$n = 7$	N	Reference energy	Ref.	Difference
1	2^2S	596	-14.323 468	991	-14.323 769	13944	-14.324 763 176 790 43(22)	[6]	994.6
3	3^2S	596	-13.921 529	991	-13.921 830	10000	-13.922 789 268 544 2	[29]	959.2
6	4^2S	596	-13.797 444	991	-13.797 754	1888	-13.798 716 609 2	[44]	962.8
10	5^2S	596	-13.743 267	991	-13.743 655	1091	-13.744 631 82	[45]	977.0
15	6^2S	596	-13.714 814	991	-13.715 222	2058	-13.716 286 24	[45]	1064.1
21	7^2S	596	-13.689 753	991	-13.697 421				
					$n = 8$				
28	8^2S			991	-13.684 764				
2	2^2P	849	-14.177 210	1430	-14.177 409	10000	-14.179 333 293 342 7	[29]	1924.4
4	3^2P	849	-13.883 174	1430	-13.883 425		-13.885 15	[46]	1725.3
7	4^2P	849	-13.781 745	1430	-13.781 975	1021	-13.783 518 3	[47]	1543.5
11	5^2P	849	-13.735 200	1430	-13.735 466		-13.737 18	[46]	1714.1
19	6^2P	849	-13.710 140	1430	-13.710 331		-13.712 06	[46]	1729.2
26	7^2P			1430	-13.695 228				
5	3^2D	646	-13.876 261	1056	-13.876 447	841	-13.877 871 0	[48]	1424.3
9	4^2D	646	-13.778 890	1056	-13.779 084	841	-13.780 514 4	[48]	1430.8
14	5^2D	646	-13.733 841	1056	-13.734 024	841	-13.735 455 4	[48]	1431.8
20	6^2D	646	-13.709 377	1056	-13.709 538				
27	7^2D			1056	-13.694 804				
8	4^2F	286	-13.779 403	532	-13.779 946				
13	5^2F	286	-13.734 363	532	-13.734 924				
18	6^2F	286	-13.709 788	532	-13.710 457				
25	7^2F			532	-13.695 579				
			$n = 7$		$n = 8$				
12	5^2G	395	-13.734 819	694	-13.735 021				
17	6^2G	395	-13.710 358	694	-13.710 575				
24	7^2G	395		694	-13.695 806				
16	6^2H	272	-13.710 376	519	-13.710 578				
23	7^2H	272	-13.695 613	519	-13.695 828				
22	7^2I			350	-13.695 844				

TABLE VI. Calculated Hy-CI energies of the ground S state and first S , P , and D excited states of Li atom. Convergence of the calculations and comparison with energy values of the literature are shown. n is the ordering number of the states. N is the number of symmetry-adapted configurations. All energies are given in a.u., while Difference refers to the energy differences between the present and the reference energies in microhartrees (1×10^{-6} a.u.).

No.	State	N	$n = 4$	N	$n = 5-7$	N	Reference energy	Ref.	Difference
1	2^2S	309	-7.478 053 222	693	-7.478 058 969	34020	-7.478 060 323 910 146 894	[3]	1.3
3	3^2S	307	-7.354 078 275	549	-7.354 093 706	34020	-7.354 098 421 444 364 045	[3]	4.7
6	4^2S	252	-7.318 481 008	591	-7.318 517 759	34020	-7.318 530 845 998 906 901	[3]	13.
10	5^2S			718	-7.303 512 964	34020	-7.303 551 579 226 734 650	[3]	38.6
15	6^2S			491	-7.295 739 603	34020	-7.295 859 510 844 131 039	[3]	120.0
					$n = 8$				
24	7^2S			506	-7.291 085 910	17072	-7.291 392 273 116	[2]	306.2
28	8^2S			816	-7.288 391 657				
2	2^2P	381	-7.410 134 123	616	-7.410 149 407	32200	-7.410 156 532 652 370	[3]	7.1
4	3^2P	530	-7.337 055 167	766	-7.337 113 796	7000	-7.337 151 707 93	[4]	37.9
7	4^2P	466	-7.311 724 861	752	-7.311 811 529	7000	-7.311 889 059 38	[4]	77.5
13	5^2P			750	-7.300 137 068	7000	-7.300 288 164 88	[4]	151.1
19	6^2P			847	-7.293 967 122	7000	-7.294 020 052 93	[4]	52.9
					$n = 8$				
26	7^2P			502	-7.289 814 402				
5	3^2D	188	-7.335 505 135	490	-7.335 512 623	32760	-7.335 523 543 524 685	[3]	10.9
8	4^2D	176	-7.311 192 543	187	-7.311 211 047	4000	-7.311 189 578 43	[5]	-21.5
14	5^2D	273	-7.298 186 482	509	-7.299 889 424	4000	-7.299 927 555 94	[5]	38.1
20	6^2D			271	-7.293 697 654	4000	-7.293 810 713 64	[5]	113.1
					$n = 8$				
27	7^2D			423	-7.289 806 792	4000	-7.290 122 856 24	[5]	324.1

calculations is ≈ 1 mhartree (1×10^{-3} a.u.). Note that the F , G , H , and I states calculated with the CI method are reported here.

For Hy-CI calculations, we employed the same blocks of configurations as in the CI calculations (see Table I) and added blocks of these configurations multiplied by one

TABLE VII. Calculated Hy-CI energies of the ground S state and first S , P , and D excited states of the Be^+ ion. Convergence of the calculations and comparison with energy values of the literature are shown here. n is the ordering number of the states. N is the number of symmetry-adapted configurations. All energies are given in a.u., while Difference refers to the energy differences in microhartrees (1×10^{-6} a.u.).

No.	State	N	$n = 4$	N	$n = 5,7$	N	Reference energy	Ref.	Difference
1	2^2S	514	-14.324 757 377	1028	-14.324 761 678	13944	-14.324 763 176 790 150	[6]	1.5
3	3^2S	502	-13.922 759 980	1199	-13.922 784 968	10000	-13.922 789 268 554 2	[29]	4.3
6	4^2S	409	-13.798 520 453	757	-13.798 706 849	1888	-13.798 716 609 2	[44]	9.8
10	5^2S			698	-13.744 580 355	1940	-13.744 631 82	[45]	51.5
14	6^2S			649	-13.716 223 859	2058	-13.716 286 24	[45]	62.4
18	7^2S			810	-13.699 298 491				
					$n = 8$				
28	8^2S			556	-13.687 885 004				
2	2^2P	373	-14.179 314 875	616	-14.179 327 999	10000	-14.179 333 293 342 7	[29]	5.3
4	3^2P	499	-13.885 035 680	707	-13.885 115 345		-13.885 15	[46]	34.7
7	4^2P	352	-13.783 432 326	582	-13.783 574 124	1021	-13.783 518 3	[47]	-56.1
11	5^2P			788	-13.736 854 458		-13.737 18	[46]	326
16	6^2P			1232	-13.711 935 268		-13.712 06	[46]	124.7
					$n = 8$				
20	7^2P			503	-13.696 356 527				
5	3^2D	265	-13.878 005 890	426	-13.878 041 021	841	-13.877 871 0	[48]	-170.0
9	4^2D	230	-13.779 724 788	450	-13.780 663 883	841	-13.780 514 4	[48]	-149.4
13	5^2D	250	-13.728 658 182	354	-13.735 539 056	841	-13.735 455 4	[48]	-83.7
17	6^2D			444	-13.710 204 495				
					$n = 8$				
27	7^2D			1009	-13.695 586 302				

TABLE VIII. The total energies of the S , P , D , F , G , H , and I states of the Li atom (in a.u.) ordered by their energy. The bound states lay below the ionization threshold of the Li^+ ion, which in nonrelativistic values is $-7.279\,913\,412\,669\,305\,964\,918\,10(15)$ a.u. [39].

No.	State	$E(\text{FCI})$	$E(\text{Hy-CI})$	Reference energy	Ref.
1	2^2S	-7.477 20(1)	-7.478 060(2)	-7.478 060 323 910 147(1)	[3]
2	2^2P	-7.408 70(9)	-7.410 150(6)	-7.410 156 532 652 41(4)	[3]
3	3^2S	-7.353 25(1)	-7.354 095(2)	-7.354 098 421 444 37(1)	[3]
4	3^2P	-7.335 70(4)	-7.337 120(7)	-7.337 151 707 93	[4]
5	3^2D	-7.334 20(9)	-7.335 520(8)	-7.335 523 543 524 688(3)	[3]
6	4^2S	-7.317 70(3)	-7.318 520(3)	-7.318 530 845 998 91(1)	[3]
7	4^2P	-7.310 40(2)	-7.311 820(9)	-7.311 889 059 38	[4]
8	4^2D	-7.309 80(4)	-7.311 220(9)	-7.311 189 578 43(200)	[5]
9	4^2F	-7.309 60(9)			
10	5^2S	-7.302 70(2)	-7.303 51(3)	-7.303 551 579 226 77(4)	[3]
11	5^2G	-7.299 50(7)			
12	5^2F	-7.299 40(6)			
13	5^2P	-7.298 90(10)	-7.300 20(7)	-7.300 288 164 88	[4]
14	5^2D	-7.298 60(10)	-7.299 91(1)	-7.299 927 555 94(300)	[5]
15	6^2S	-7.296 00(6)	-7.295 80(6)	-7.295 859 510 844 19(6)	[3]
16	6^2H	-7.293 40(8)			
17	6^2G	-7.293 30(1)			
18	6^2F	-7.293 30(9)			
19	6^2P	-7.293 60(5)	-7.294 00(4)	-7.294 020 052 93	[4]
20	6^2D	-7.292 40(1)	-7.293 70(3)	-7.293 810 713 64(500)	[5]
21	7^2I	-7.289 71(7)			
22	7^2H	-7.289 70(7)			
23	7^2G	-7.289 65(4)			
24	7^2S	-7.285 70(5)	-7.291 10(15)	-7.291 392 276(3)	[2]
25	7^2F	-7.289 45(5)			
26	7^2P	-7.289 8(5)	-7.290 00(9)		
27	7^2D	-7.289 8(10)	-7.289 90(10)	-7.290 122 856 24(2000)	[5]
28	8^2S	-7.286 7(10)	-7.288 50(10)		

interelectronic coordinate at a time, i.e., $\text{CI} \times (1 + r_{12} + r_{13} + r_{23})$. Details on the selection of configurations are given above. Hy-CI calculations up to the basis $n = 6-8$ were performed.

It is important to note that in Hy-CI calculations it is usually not necessary to use basis sets as large as in CI calculations, since the wave function expansion converges faster to the exact solution. This is due to the explicit inclusion of the interelectronic coordinate in the wave function. In contrast, in the CI method the interelectronic coordinate is not explicitly considered, and its effect is replaced by the use of high angular momentum orbitals. In short, for Hy-CI calculations high angular momentum orbitals ($l \geq 3$) are not required to achieve an accuracy in the microhartree regime (1×10^{-6} a.u.), which is the purpose of this paper. Note that highly accurate Hy-CI calculations can be afforded if using long wave-function expansions; see the benchmark energy values for the 6^2S and 7^2S states of Li atom [2].

The bound, rotationally excited F , G , H , and I states have never been calculated with the use of the Hy-CI method due to the complexity of the related problems. Some recent developments, however, make such calculations possible. For instance, in our computer program, the electronic integrals are defined for every l quantum number, but the kinetic energy integrals are currently restricted to $l \geq 2$, see Ref. [34]. The theoretical and computational implementation of higher

quantum numbers is somewhat cumbersome and will be reported elsewhere.

The nonrelativistic total energies of the four and/or five lowest bound states of S , P , and D symmetry are now known to high accuracy, whereas other similar states have been determined to less accuracy, since in these cases we have used shorter trial wave functions (see Tables VI and VII).

In the Hy-CI calculations of the Li atom (see Table VI) the maximum achieved accuracy is of a few microhartrees (1×10^{-6} a.u.) for the ground state and first S , P , and D excited states. For higher excited states the accuracy is slightly lower. For highly excited bound states it is less than 1 mhartree (1×10^{-3} a.u.), as far as values for these states were known. This is because the use of a set of two exponents for all configurations is not as appropriate for highly excited states as for the ground and low-excited bound states. For instance, we determined the total energy of the 8^2S ($E = -7.288\,391\,657$ a.u.) state. By performing analogous calculations for the 4^2D state we obtained the total energy which is the best to date for this state $E = -7.311\,211\,047$ a.u.

For the Be^+ ion, the maximal accuracy is slightly better, which is directly related with the larger nuclear charge (see Table VII) and more compact electron wave function. For the ground state and low excited states of the Li atom we obtained

TABLE IX. The total energies of the S , P , D , F , G , H , and I states of the Be^+ ion ordered by their total energies. All these bound states are stable, since their total energies are below the ionization threshold which coincide with the nonrelativistic energy of the Be^{2+} ion $E_{\text{tr}} = -13.655\,566\,238\,423\,586\,702\,078\,10(15)$ a.u. [39].

No.	State	$E(\text{FCI})$	$E(\text{Hy-CI})$	Ref. energy	Ref.
1	2^2S	-14.323 80(3)	-14.324 763(2)	-14.324 763 176 790 43(22)	[6]
2	2^2P	-14.177 43(2)	-14.179 330(3)	-14.179 333 293 42(3)	[29]
3	3^2S	-13.921 90(3)	-13.922 786(2)	-13.922 789 268 570(10)	[29]
4	3^2P	-13.883 50(7)	-13.885 120(5)	-13.885 15	[46]
5	3^2D	-13.876 50(5)	-13.878 050(5)	-13.877 871 0	[48]
6	4^2S	-13.797 80(5)	-13.798 710(4)	-13.798 716 609 2	[44]
7	4^2P	-13.782 00(2)	-13.783 580(5)	-13.783 518 3	[47]
8	4^2F	-13.778 00(5)			
9	4^2D	-13.779 10(2)	-13.780 70(4)	-13.780 514 4	[48]
10	5^2S	-13.743 70(4)	-13.744 60(2)	-13.744 631 82	[45]
11	5^2P	-13.735 50(3)	-13.736 90(5)	-13.737 18	[46]
12	5^2G	-13.735 10(8)			
13	5^2F	-13.735 00(7)			
14	5^2D	-13.734 10(7)	-13.735 60(4)	-13.735 455 4	[48]
15	6^2S	-13.715 30(8)	-13.716 25(3)	-13.716 286 24	[45]
16	6^2H	-13.710 65(2)			
17	6^2G	-13.710 60(3)			
18	6^2F	-13.710 50(4)			
19	6^2P	-13.710 20(6)	-13.712 00(7)	-13.712 06	[46]
20	6^2D	-13.709 60(6)	-13.710 25(5)		
21	7^2S	-13.697 50(8)	-13.699 30(8)		
22	7^2I	-13.695 86(2)			
23	7^2H	-13.695 85(2)			
24	7^2G	-13.695 83(2)			
25	7^2F	-13.695 60(2)			
26	7^2P	-13.695 3(7)	-13.696 40(5)		
27	7^2D	-13.694 9(10)	-13.695 60(11)		
28	8^2S	-13.684 8(3)	-13.688 00(12)		

an accuracy of few microhartrees (1×10^{-6} a.u.), using less than 1000 configurations, whereas the best calculations in the literature use up to 14 000 configurations.

The benchmarks obtained for Be^+ ion are the 4^2P state ($E = -13.783\,574\,124$ a.u.), 3^2D state ($E = -13.878\,041\,021$ a.u.), 4^2D state ($E = -13.780\,663\,883$ a.u.), and 5^2D state ($E = -13.735\,537\,780$ a.u.). The newly calculated states are 7^2S ($E = -13.699\,298\,491$ a.u.), 8^2S ($E = -13.687\,885\,004$ a.u.), 7^2P ($E = -13.696\,356\,527$ a.u.), 6^2D ($E = -13.710\,204\,495$ a.u.), and 7^2D ($E = -13.695\,586\,302$ a.u.). The dissociation threshold for the three-electron ${}^\infty\text{Be}^+$ ion is $\approx -13.655\,566\,238\,423\,586\,702\,079\,65(25)$ a.u. [39]. This value coincides with the total energy of the ground 1^1S state of a Be^{2+} ion with an infinitely heavy nucleus. The optical spectra of the Li atom and Be^+ ions can be found in Ref. [40]. The optical spectrum of the Li atom determined in this study is in good agreement with the spectrum of the Li atom shown in that work.

We obtained this accuracy with less than 1% of the configurations used in the most highly accurate calculations reported. All calculated states are ordered by their energy and presented in Tables VIII and IX. The total energies of these states are below the corresponding threshold energy (or ionization energy) for the three-electron atomic systems considered here.

V. CONCLUSIONS AND PERSPECTIVES

We have determined the total energies of 28 bound states in the Li atom and Be^+ ion, respectively. The variational wave functions of the S , P , D , F , G , H , and I bound states in these three-electron atomic systems were constructed with the use of the CI and Hy-CI methods. The procedure consisted in the appropriate selection of configurations and optimization of one set of orbital exponents for every state. The total energies of the low-lying states are microhartree accurate (1×10^{-6} a.u.), while for excited states the accuracy is $\approx 1 \times 10^{-4} - 10^{-5}$ a.u. We have obtained several benchmarks and reported the energy of some highly excited states. These wave functions are convenient for the calculation of properties. Consequently, these wave functions have been used for the calculation of the transition probabilities during nuclear β decay, where wave functions of very good quality are necessary to describe the atomic effects during nuclear reactions [41–43]. Our future plan include this systematic method of calculations to determine ground and excited states of the following atoms and isoelectronic ions in the periodic table, such as Be, B, and C.

The results of our study are of great interest in various applications which includes different problems in astrophysics (e.g., to analyze the emission spectra of the hot Wolf-Rayet stars [49]), physics of stellar and laboratory plasmas, physics

of few-body systems, etc. Analogous calculations of various rotationally and “vibrationally” excited (bound) states in two-electron helium atom were conducted by Drake [50]. It is clear that the total energies reported by Drake [50] are more accurate, but we consider a much more complicated case of bound states in three-electron atoms and ions. Note also that the spectra of the two-electron atoms and ions include two independent series, singlet and triplet, while for three-electron atoms or ions only doublet spin states belong to the actual discrete spectrum. All quartet spin states of the three-electron atoms or ions are in the continuum; i.e., they are not truly bound states and any interaction (such as spin-spin interactions) that breaks electron permutation symmetry will force the quadruplet states to decay. Here we do not want

to discuss the quadruple states in the three-electron atomic systems, since (1) they are not truly bound states and (2) our method does not allow to analyze the properties of such states, which can be observed as quasibound states at very special experimental conditions.

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