PHYSICAL REVIEW A **80**, 042511 (2009)

Calculations of polarizabilities and hyperpolarizabilities for the Be$^+$ ion

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(Received 16 August 2009; published 20 October 2009)

The polarizabilities and hyperpolarizabilities of the Be$^+$ ion in the $2\,^2S$ state and the $2\,^2P$ state are determined. Calculations are performed using two independent methods: (i) variationally determined wave functions using Hylleraas basis set expansions and (ii) single electron calculations utilizing a frozen-core Hamiltonian. The first few parameters in the long-range interaction potential between a Be$^+$ ion and a H, He, or Li atom, and the leading parameters of the effective potential for the high-L Rydberg states of beryllium were also computed. All the values reported are the results of calculations close to convergence. Comparisons are made with published results where available.

DOI: 10.1103/PhysRevA.80.042511 PACS number(s): 31.15.ac, 31.15.ap, 34.20.Cf

I. INTRODUCTION

Studies of the Be$^+$ ion are of interest due to its importance in a number of applications. First, the Be$^+$ ion is used as an auxiliary ion to sympathetically cool other atomic or ionic species [1,2] that cannot be directly laser cooled due to the lack of closed optical transitions. Second, the Be$^+$ ion can combine with other atoms or neutral molecules to form molecular ions, such as BeH$^+$ [3–6], and the study of the long-range interaction between a Be$^+$ ion and atoms or molecules may open new routes for the study of state-selective chemical reactions relevant to astrophysics [3]. Third, investigations of Be$^+$ ion collisions with rare gases would be useful in the study of ion-atom Feshbach resonances [7], pressure broadening of alkaline-earth-metal ions [8], and in studies of excitation spectroscopy of the collision [9,10]. Fourth, since beryllium has a number of isotopes, studies of the Be$^+$ ion could potentially be used to determine the nuclear charge radii of beryllium isotopes [11]. Finally, there is interest in studying the spectra of the alkaline-earth-metal atoms in high angular momentum Rydberg states. Experimental investigations have been made on a number of atoms [12–15] with a view to determining the polarizabilities of the singly ionized parent ion. These experiments measure the high (n,L) energy splitting and then use a polarization model to extract the polarizabilities. Recent calculations [16] have shown the polarization model to be sensitive to nonadiabatic effects. The Be$^+$ ion would be a useful candidate for a validation experiment since it should be less sensitive to adiabatic effects and its polarizabilities can be calculated to very high precision.

The above physical phenomena are influenced by the properties of the Be$^+$ ion, and in particular the polarizabilities and hyperpolarizabilities. There have been several calculations of the Be$^+$ ion polarizabilities reported in the literature. These include the work by Adelman and Szabo [17] using the Coulomb-like approximation, the calculation by Pipin and Woznicki [18] using the variation-perturbation approach with a combined Hylleraas-configuration interaction (CI) basis set, the calculation by Patil and Tang [19] using the valence electron binding energy to construct wave functions constrained to have the correct long-range asymptotic behavior, and finally the large basis full core plus configuration interaction (FCCI) calculations by Wang and collaborators [20–25]. However, there have been no calculations reported on the polarizabilities and hyperpolarizabilities for the Be$^+$ ion excited states.

In this paper, the polarizabilities, hyperpolarizabilities and some long-range ion-atom dispersion coefficients involving Be$^+$ ion are computed with two independent methods. First, oscillator strengths for many low-lying transitions are determined. Next, the polarizabilities and hyperpolarizabilities for the $2\,^2S$ state and $2\,^2P$ state of Be$^+$ ion are computed variationally using expansions of the wave functions in Hylleraas bases. The same set of long-range parameters is also computed using a fixed core plus semiempirical polarization potential to describe the valence electron. The agreement between the two different calculations will be seen to be excellent. The long-range dispersion interactions between Be$^+$ ion and the H, He, or Li atoms are given and once again the agreement between the two sets of calculations is excellent. Furthermore, we compute all the parameters needed to define a Be$^+$ ion polarization potential (including terms up to $\mathbf{r}^{-8}$) to describe the high-L Rydberg states of beryllium, where $\mathbf{r}$ is the ion-electron distance. All results of this paper are given in atomic units ($e=\hbar=m_e=1$).

II. THEORY AND METHOD

A. Hylleraas variational method

The calculations for Be$^+$ ion are very similar in style to those for Li [26,27]. In the center of mass frame, the nucleus is taken as the reference particle 0, with mass m_0 and charge q_0, r_i is the electron-nucleus distance, and $i=1,2,3$. The nonrelativistic Hamiltonian of this system can be written in the form

$$H_0 = -\sum_{i=1}^{3} \frac{1}{2\mu_i}\nabla_i^2 - \frac{1}{m_0}\sum_{i>j\geq 1}^{3} \nabla_i \cdot \nabla_j + q_0 \sum_{i=1}^{3} \frac{q_i}{r_i} + \sum_{i>j\geq 1}^{3} \frac{q_i q_j}{r_{ij}}, \tag{1}$$

where $r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|$ is the distance between electrons i and j, q_i are the charge of the three electrons, and $\mu_i=m_i m_0/(m_i+m_0)$ is the reduced mass between the ith electron and the nucleus. In the present paper, all the calculations are done in the infinite nuclear mass approximation.

Significant progress has been made recently in variational calculations for three-electron systems by using multiple basis sets in Hylleraas coordinates [28,29]. These have the functional form,

$$\phi = r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{j_{12}} r_{23}^{j_{23}} r_{31}^{j_{31}} e^{-\alpha r_1 - \beta r_2 - \gamma r_3} \times \mathcal{Y}^{LM_L}_{(\ell_1\ell_2)\ell_{12},\ell_3}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2,\hat{\mathbf{r}}_3)\chi(1,2,3), \tag{2}$$

where $\mathcal{Y}^{LM_L}_{(\ell_1\ell_2)\ell_{12},\ell_3}$ is a vector-coupled product of spherical harmonics to form an eigenstate of total angular momentum L and projection M_L, and $\chi(1,2,3)$ is the three-electron spin function. The variational wave function is a linear combination of antisymmetrized basis functions ϕ. With some truncations to avoid potential numerical linear dependence, all terms in Eq. (2) are included such that

$$j_1 + j_2 + j_3 + j_{12} + j_{23} + j_{31} \leq \Omega, \tag{3}$$

where Ω is an integer, and the convergence for the energy eigenvalue is studied by progressively increasing Ω.

For the He atom, taking the nucleus as the reference particle 0, the electron is labeled as particle 1 and the other electron is labeled as particle 2. The wave functions are expanded in terms of the explicitly correlated basis set in Hylleraas coordinates,

$$\phi = r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2} \mathcal{Y}^{LM}_{\ell_1 \ell_2}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2). \tag{4}$$

For the hydrogen atom, we use a basis set of form

$$\phi = r^{\ell} e^{-\beta r/2} L_n^{(2\ell+2)}(\beta r)\mathcal{Y}_{\ell m}(\hat{\mathbf{r}}), \tag{5}$$

where $L_n^{(2\ell+2)}(\beta r)$ is the generalized Laguerre polynomial and the parameter β is chosen to be $\beta=2/(\ell+1)$. This basis set has been proven to be numerically stable as the size of the basis set is increased.

B. Single electron model

The detailed description of the procedure used to construct the frozen-core Hamiltonian and the semiempirical polarization potential can be found in previous works by Mitroy and collaborators [16,30,31]. Accordingly, only the briefest description is given here.

Initially, a Hartree-Fock calculation of the Be$^+$ ion ground state was performed. The core orbitals were then fixed, and a semiempirical core polarization potential was added to the Hamiltonian. The core dipole polarizability was taken to be 0.0523 [30]. The cutoff parameters in the semiempirical core polarization potential were $\rho_0=0.941$, $\rho_1=0.895$, $\rho_2=1.200$ with all other ρ_L set to 1.00 [30]. These values were chosen to reproduce the binding energies of the low-lying states.

The low-lying states and pseudocontinuum states were obtained by diagonalizing the fixed core Hamiltonian in a large basis of Laguerre type orbitals. Typically, there were about 50 orbitals for each value of the valence angular momentum. This is large enough to eliminate the basis as a significant source of error.

The multipole matrix elements and oscillator strengths were computed with a modified transition operator [30]. The adjustable parameter in the modified multiple operator was set to $\rho=1.00$. Core excitations are included in the dispersion parameter calculation. Oscillator strength distributions were constructed from independent estimates of the core polarizabilities ($\alpha_2=0.01\,532$ [30] and $\alpha_3=0.01\,125$ [32]). The calculations using this approach are termed the Hartree-Fock plus core polarization (HFCP) model.

The dispersion coefficient calculations involving H and He used matrix element lists that were generated using basis functions that were similar (but not identical) in construction to Eqs. (4) and (5). The matrix element lists for the Li atom came from a one electron model as described in Ref. [33].

C. Polarizabilities

Using perturbation theory, the adiabatic long-range interaction potential for an ion-atom system up to the R^{-8} term can be written [34] as

$$V_{ab}(R) = -\frac{1}{2}Q_a^2 \sum_{\ell=1}^{3} \frac{\alpha_\ell^{(b)}}{R^{2\ell+2}} - \sum_{n=3}^{4} \frac{C_{2n}}{R^{2n}}, \tag{6}$$

where $Q_a=\Sigma_i Q_i$ is the total charge of the ion a, $\alpha_\ell^{(b)}$ is the 2^ℓ-pole static polarizability for the atom b, R is the distance between the ion and the atom, and the C_{2n} parameters are the dispersion coefficients. The first term in Eq. (6) is the polarization interaction, which does not lead to a frequency shift between the different states of the ion. The second term is the dispersion interaction, which can lead to a frequency shift between two different ion states when the ion is immersed in a buffer gas. From Eq. (6), we see that the establishment of the interaction potential $V_{ab}(R)$ accurate to R^{-8} requires the static polarizabilities α_1, α_2, and α_3 for the atom b, and the dispersion coefficients C_6 and C_8 between ion a and atom b. Once we have obtained the oscillator strength spectra between the ground states and the intermediate states for the H, He, Li, and Be$^+$ ion systems, we can calculate the Be$^+$ ion polarizabilities, and the dispersion coefficients for various combinations of these particles. The detailed derivation of the formulae for calculating the polarizabilities, hyperpolarizabilities and dispersion coefficients in Hylleraas coordinates can be found in the Ref. [26].

For the high-L Rydberg states of an atom or an ion, where a single electron is in highly excited state but still moves in the field of a spherically symmetric core, the polarization interaction between the core and a single Rydberg electron leads to the effective potential [12,13,16,35,36],

$$V_{\text{eff}}(\mathbf{r}) = -\frac{A_4}{\mathbf{r}^4} - \frac{A_6}{\mathbf{r}^6} - \frac{A_7}{\mathbf{r}^7} - \frac{A_8}{\mathbf{r}^8} - \frac{A_{8L}L(L+1)}{\mathbf{r}^8} + \cdots, \quad (7)$$

where $\mathbf{r}$ is the radial coordinate of the Rydberg electron and the coefficients A_n are properties of the free ion core. Comparisons with high precision variational calculations of the Rydberg states for the few-body systems, He [37], Li [21], and H_2 [38] have been made. This functional form has also been used to analyze the fine structure spectrum of the Rydberg states of neutral Mg and Ba, resulting in estimates of the dipole polarizabilities of the alkaline-earth-metal ions Mg^+ and Ba^+ ground states [12,14,31].

According to the definitions given previously [31,35,39], the leading coefficient A_4 is half the size of the static dipole polarizability,

$$A_4 = \frac{\alpha_1}{2}, \quad (8)$$

with

$$\alpha_1 = \frac{8\pi}{9}\sum_n \frac{|\langle n_0 0\|T_1\|n1\rangle|^2}{E_n - E_0}. \quad (9)$$

The notation $|nL\rangle$ indicates the intermediate state with main quantum number n and angular momentum number L, and T_1 is the dipole transition operator, which satisfies the general expression for the 2^ℓ-pole transition operator in the center of mass frame,

$$T_\ell = \sum_{i=1}^{3} q_i r_i^\ell Y_{\ell 0}(\hat{\mathbf{r}}_i). \quad (10)$$

The next term A_6 is composed of two separate terms,

$$A_6 = \frac{\alpha_2 - 6\beta_1}{2}, \quad (11)$$

where α_2 is the quadrupole polarizability and β_1 is the first-order nonadiabatic correction to dipole polarizability. They are defined as

$$\alpha_2 = \frac{8\pi}{25}\sum_n \frac{|\langle n_0 0\|T_2\|n2\rangle|^2}{E_n - E_0}, \quad (12)$$

$$\beta_1 = \frac{4\pi}{9}\sum_n \frac{|\langle n_0 0\|T_1\|n1\rangle|^2}{(E_n - E_0)^2}. \quad (13)$$

The $\mathbf{r}^{-7}$ term A_7 also comes from two parts, namely,

$$A_7 = -\frac{5\eta + 16q\delta_1}{10}, \quad (14)$$

where q is the charge on the core. η arises from third-order perturbation theory and it can be expressed as

$$\eta = \frac{32\pi\sqrt{10\pi}}{225}\sum_{m,n}\frac{\langle n_0 0\|T_1\|m1\rangle\langle m1\|T_1\|n2\rangle\langle n2\|T_2\|n_0 0\rangle}{(E_m - E_0)(E_n - E_0)} + \frac{16\pi\sqrt{6\pi}}{135}\sum_{m,n}\frac{\langle n_0 0\|T_1\|m1\rangle\langle m1\|T_2\|n1\rangle\langle n1\|T_1\|n_0 0\rangle}{(E_m - E_0)(E_n - E_0)}, \quad (15)$$

and δ_1 is the second-order nonadiabatic correction to the dipole polarization energy,

$$\delta_1 = \frac{4\pi}{18}\sum_n \frac{|\langle n_0 0\|T_1\|n1\rangle|^2}{(E_n - E_0)^3}. \quad (16)$$

Quite a few terms contribute to A_8,

$$A_8 = \frac{\alpha_3 - 15\beta_2 + \epsilon - \alpha_1\beta_1 + 72\delta_1}{2}. \quad (17)$$

The octupole polarizability α_3 is computed by

$$\alpha_3 = \frac{8\pi}{49}\sum_n \frac{|\langle n_0 0\|T_3\|n3\rangle|^2}{E_n - E_0}, \quad (18)$$

while β_2 comes from the first-order nonadiabatic correction part to the quadrupole polarization energy, and is defined as

$$\beta_2 = \frac{4\pi}{25}\sum_n \frac{|\langle n_0 0\|T_2\|n2\rangle|^2}{(E_n - E_0)^2}. \quad (19)$$

The term ϵ is defined

$$\epsilon = \frac{32\pi^2}{81}\sum_{m,n}\frac{|\langle n_0 0\|T_1\|m1\rangle\langle m1\|T_1\|n0\rangle|^2}{(E_m - E_0)^2(E_n - E_0)} + \frac{64\pi^2}{405}\sum_{m,n}\frac{|\langle n_0 0\|T_1\|m1\rangle\langle m1\|T_1\|n2\rangle|^2}{(E_m - E_0)^2(E_n - E_0)}. \quad (20)$$

The hyperpolarizability γ_0 of the ground state, and coefficients ϵ, α_1, β_1 are related by the identity $\gamma_0 = 12(\epsilon - \alpha_1\beta_1)$. The last term A_{8L} is nonadiabatic in origin and defined by

$$A_{8L} = \frac{18\delta_1}{5}. \quad (21)$$

For excited states, the working expressions for the evaluation of the polarizabilities α_1, α_1^T, α_2, and α_3 and hyperpolarizabilities γ_0 and γ_2 are given in Tang *et al.* [26]. These expressions are quite lengthy and they are not reproduced here.

D. Dispersion interactions

The dispersion interaction, between two atoms, A and B, for the Hylleraas wave functions was calculated from tabulated lists of matrix elements using sum rules [26]. For the case of C_6 involving two S-state atoms, one can write the sum rule

$$C_6 = \frac{3}{2}\sum_{mn}\frac{f_{0m}^A f_{0n}^B}{\Delta E_{m0}^A \Delta E_{n0}^B(\Delta E_{m0}^A + \Delta E_{n0}^B)} \quad (22)$$

The sum is over all states of P^o-symmetry. The absorption oscillator strength, f_{0n}, for a dipole transition from $0 \rightarrow n$,

TABLE I. Convergence of the Hylleraas calculation of the nonrelativistic energy (in atomic units) for the 2^2S state of Be^+ ion.

Ω	No. of terms	$E(\Omega)$	$E(\Omega)-E(\Omega-1)$	$R(\Omega)$
8	1589	−14.324763166358	−0.000000051721	8.211
9	2625	−14.324763174596	−0.000000008238	6.278
10	4172	−14.324763176309	−0.000000001713	4.809
11	6412	−14.324763176663	−0.000000000354	4.839
Extrap.		−14.324763176736(73)		

with an energy difference of $\Delta E_{n0}=E_0-E_n$, is most conveniently defined in the present context [27,30] as

$$f_{0n}=\frac{2|\langle\psi_0;L_0||r\mathbf{C}^1(\hat{\mathbf{r}})||\psi_n;L_n\rangle|^2\Delta E_{n0}}{3(2L_0+1)}. \tag{23}$$

In this expression for the HFCP method, L_0 is the ground-state orbital angular momentum, and $r\mathbf{C}^1(\hat{\mathbf{r}})=\sqrt{\frac{4\pi}{3}}r\mathbf{Y}^1(\hat{\mathbf{r}})$ is the operator for a dipole transition just for one electron. Explicit expressions for C_8, and C_{10}, and for other symmetries can be found in [26].

The dispersion interaction calculations for the HFCP wave functions utilized the completely general procedures outlined by Zhang and Mitroy [40,41]. These calculations utilize sum rules involving lists of reduced matrix elements of the multipole operator $r^k\mathbf{C}^k$ multiplied by angular recoupling factors. They are effectively equivalent to Eq. (22) and the expressions in [26] despite the differences how the calculations are actually carried out.

III. RESULTS AND DISCUSSION

A. Energies and oscillator strengths of Be^+ ion

Table I shows the convergence study for the nonrelativistic energy of the Be^+ ion ground state as the size of the Hylleraas basis set is enlarged. The ratio $R(\Omega)$ is defined by

$$R(\Omega)=\frac{E(\Omega-1)-E(\Omega-2)}{E(\Omega)-E(\Omega-1)}. \tag{24}$$

The extrapolation was done by assuming that the ratio would stay constant around $R(\Omega)=4.839$. It is clear from Table I that the energy converges to high precision as the number of terms is progressively increased. The final nonrelativistic energy is accurate to about 11 significant figures for the ground state and the uncertainty is set to be equal to the extrapolation correction. The nonrelativistic theoretical energies for other low-lying states of Be^+ ion are tabulated and compared with experimental binding energies in Table II. Binding energies from the HFCP calculations are also listed.The Hylleraas binding energies, which do not include finite mass and relativistic effects, are generally in good agreement with the experimental binding energies. The finite-mass effect will be about 0.001% and will probably act to decrease the magnitude of the binding energy. The largest discrepancy for the 2^2S state is due entirely to relativistic effects (see Table III of [29]), which contribute about 0.007% of the final value.

Table III lists the oscillator strengths for a number of the Be^+ ion dipole transitions involving low-lying states. The final values for the Hylleraas calculations are obtained with an extrapolation procedure similar to that for the energy. Once again the uncertainty in the oscillator strength is assigned to be equal to the magnitude of the extrapolation correction. It is evident from Table III that there is excellent agreement between the Hylleraas and HFCP calculations. The largest discrepancy between the two calculations is only about 0.1% (for the $3\,^2P\rightarrow 3\,^2D$ transition). The oscillator strengths from the Hylleraas calculation could be used to improve the National Institute of Standards and Technology (NIST) tabulations [42,43].

The Hylleraas oscillator strength for the $2\,^2S\rightarrow 2\,^2P$ transition is accurate to about seven significant figures and is compatible with an earlier Hylleraas calculation by Yan *et al.* [44]. Some earlier large scale *ab initio* calculations also gave oscillator strengths that are compatible with the present Hylleraas calculation for this transition. These include the multiconfiguration Hartree-Fock (MCHF) calculation of Godefroid *et al.* [45] and the FCCI calculation of Chung *et al.*

TABLE II. Theoretical nonrelativistic energies and experimental energies of the low-lying states for the Be^+ ion, (in atomic units). The numerical uncertainty of the theoretical energies are given in brackets. The experimental valence binding energies are taken from the National Institute of Standards database [47,48]. The ground-state energy for the Be^{2+} ion was taken from Ref. [49].

State	Hylleraas	$E_{\text{Hylleraas}}-E(\mathrm{Be}^{2+})$	HFCP	Experiment	Ref. [29]
$2\,^2S$	−14.324763176736(73)	−0.669196938312	−0.669250	−0.669247	−0.66924793(2)
$2\,^2P$	−14.17933329329(24)	−0.52376705486	−0.523755	−0.523769	−0.52376988(2)
$3\,^2S$	−13.9227892683(5)	−0.2672230298	−0.267189	−0.267233	−0.26723367(3)
$3\,^2P$	−13.8851502898(5)	−0.2295840513	−0.229527	−0.229582	
$3\,^2D$	−13.87805405934(36)	−0.22248782091	−0.222482	−0.222478	
$4\,^2S$	−13.7987166133(8)	−0.1431503748	−0.143131	−0.143152	
$4\,^2F$	−13.780581705614(80)	−0.125015467190	−0.125015	−0.125008	
$5\,^2G$	−13.735568352173(16)	−0.080002113749	−0.080002	−0.079997	

TABLE III. Dipole oscillator strengths for the selected transitions of Be$^+$ ion.

Transition	Hylleraas	HFCP	NIST [43,42]	Exp. [46]	Other theory
$2\ ^2S \rightarrow 2\ ^2P$	0.49806736(6)	0.4985	0.505	0.54(3)	0.498067381(25) Hylleraas [44] 0.49807 MCHF [45] 0.49813 FCCI [22]
$2\ ^2S \rightarrow 3\ ^2P$	0.08316525(18)	0.0828	0.0804		0.08136 FCCI [25]
$2\ ^2P \rightarrow 3\ ^2S$	0.06434157(29)	0.0643	0.0665	0.048(5)	
$2\ ^2P \rightarrow 4\ ^2S$	0.01021583(30)	0.0102	0.010		
$2\ ^2P \rightarrow 3\ ^2D$	0.6319828(11)	0.6321	0.652		0.63199 MCHF [45] 0.63197 FCCI [23]
$3\ ^2S \rightarrow 3\ ^2P$	0.8297696(15)	0.8307			
$3\ ^2P \rightarrow 3\ ^2D$	0.08103350(17)	0.0804			
$3\ ^2P \rightarrow 4\ ^2S$	0.1345245(13)	0.1346			
$3\ ^2D \rightarrow 4\ ^2F$	1.01460194(11)	1.0146	1.01	0.66(3)	1.0146 FCCI [24]
$4\ ^2F \rightarrow 5\ ^2G$	1.34537126(12)	1.3453			

[22]. While the present oscillator strengths are reported with seven significant digits, finite-mass, and relativistic effects that are not included in the calculation could conceivably alter the oscillator strengths beginning at the fifth digit.

There have also been some high precision oscillator strengths reported for the $2\ ^2P \rightarrow 3\ ^2D$ transition. The MCHF value of Godefroid *et al.* [45] and the FCCI value of Qu *et al.* [23] agree with the Hylleraas calculation to better than four digits. Qu *et al.* [24,25] have also reported CI calculations for the $2\ ^2S \rightarrow 3\ ^2P$ and $3\ ^2D \rightarrow 4\ ^2F$ transitions and again there is agreement to better than four significant digits. The experimental oscillator strengths listed in the Table were measured using beam-foil spectroscopy [46]. These oscillator strengths have only low precision and cannot discriminate between the higher quality theoretical estimates.

B. Polarizabilities of the Be$^+$ ion

The convergence properties of the static dipole polarizability α_1, and hyperpolarizability γ_0 for the Be$^+$ ion ground state are presented in Table IV. Both of them have converged to five significant figures. The extrapolation was done by assuming that the ratio between two successive differences would stay constant as the basis size increased toward infinity. The uncertainty in the final value is set equal to the magnitude of the extrapolation correction from the explicitly calculated value computed with the basis of largest dimension.

TABLE IV. Convergence of the dipole polarizability α_1 and hyperpolarizability γ_0 for the Be$^+$ ion ground state (in atomic units). The number of intermediate states of a given angular momentum are denoted as N_S, N_P, and N_D.

(N_S,N_P)	α_1	(N_S,N_P,N_D)	γ_0
(1589,1174)	24.495332	(1589,1174,1174)	−11521.1320
(2625,2091)	24.496067	(2625,2091,2091)	−11521.3184
(4172,3543)	24.496408	(4172,3543,3543)	−11521.3196
(6412,5761)	24.496522	(6412,5761,5761)	−11521.2768
Extrap.	24.4966(1)	Extrap.	−11521.30(3)

Table V shows the convergence as a function of basis size for the scalar and tensor dipole polarizabilities α_1, α_1^T, and the hyperpolarizabilities γ_0, γ_2 for the first excited state of Be$^+$ ion. The intermediate sums in this case have contributions from doubly excited unnatural parity states with $L^\pi = 1^e$ and $L^\pi = 2^o$ (e.g., the unnatural parity 1^e state has two $\ell = 1$ electrons coupled to a total angular momentum of $L = 1$). The contribution from the unnatural parity states is usually small. For example, the unnatural parity P^e states contribution of 0.020 616 to α_1 is about 1%. The scalar dipole polarizability is converged to five significant digits, and the tensor dipole polarizability α_1^T is converged to six digits. The hyperpolarizabilities, γ_0 and γ_2 are accurate, resectively, to six and five significant figures. There was no major numerical cancellation in the hyperpolarizabilities in our calculation, in contrast to the situation that prevails for the Li hyperpolarizability, which suffers severely from cancellations in the different parts of the calculation [26].

There have been a number of accurate calculations of the multipolar polarizabilities for the Li atom in its ground or lowest excited states [26,33,50]. However, there have been fewer polarizability calculations for the Be$^+$ ion in its ground and lowest energy excited states. Table VI gives a comparison between the present results and previous calculations for the static polarizabilities of Be$^+$ ion in the $2\ ^2S$ and $2\ ^2P$ states. One of the most notable features of the Table is the very good agreement between the Hylleraas and HFCP multipole polarizabilities. The overall level of agreement is at the 0.1% level. The one exception was the static dipole polarizability of the $2\ ^2P$ state, but it should be noted that this polarizability is small due to cancellation between different terms in the oscillator strength sum. The polarizability of the Be$^+(2\ ^2P)$ state is relatively small because the Be$^+(2\ ^2P \rightarrow 2\ ^2S)$ oscillator strength is negative while all the other Be$^+(2\ ^2P \rightarrow n\ ^2L)f$ values are positive. The net effect of the

TABLE V. Convergence of the dipole polarizabilities α_1, α_1^T and the hyperpolarizabilities γ_0, γ_2 for the Be$^+$ ion in the $2\,^2P$ state (in atomic units). The number of natural parity intermediate states of a given angular momentum are denoted as N_S, N_P, N_D, and N_F. The number of unnatural parity intermediate states of a given angular momentum are denoted as $N_{P'}$ and $N_{D'}$.

$(N_S,N_P,N_D,N_{P'})$	α_1	α_1^T	$(N_S,N_P,N_D,N_F,N_{P'},N_{D'})$	γ_0	γ_2
(1589,1174,1174,1106)	2.0246197	5.85605426	(1589,1174,1174,1248,1106,1428)	10911.66561	−7372.0881
(2625,2091,2091,2002)	2.0247235	5.85601968	(2625,2091,2091,2307,2002,2640)	10913.22187	−7373.4188
(4172,3543,3543,3413)	2.0247465	5.85601425	(4172,3543,3543,4051,3413,4587)	10913.57650	−7373.6683
(6412,5761,5761,3413)	2.0247537	5.85601346	(6412,5761,5761,6806,3413,4587)	10913.57218	−7373.5698
Extrap.	2.02476(1)	5.856012(1)	Extrap.	10913.57(1)	−7373.61(5)

cancellations is a reduction in the overall size of the polarizability by a factor of five.

The Coulomb approximation polarizability [17] and the asymptotically correct wave function polarizabilities [19] achieve about 1–2% accuracy in α_1 and α_2. This is noticeably worse than any of the other polarizabilities listed in the Table. The older Hylleraas-type calculations by Pipin and Woznicki [18] used the variation-perturbation approach to estimate the polarizabilities (as opposed to oscillator strength sum rules). Their value of $\alpha_1=24.5$ [18] is compatible with the present value but not nearly as precise as the Hylleraas polarizability. The variation-perturbation calculations using the FCCI wave function [20,21] gave polarizabilities that agree with the present Hylleraas polarizabilities to better than 0.01%.

The present results for the Be$^+(2\,^2P)$ state are the only results reported for the higher order polarizabilities and the hyperpolarizabilities. Previously Mérawa and Rérat reported the calculations for α_1 and α_1^T for the Be$^+(2^2P)$ state using the time-dependent gauge-invariant method (TDGI) [51], but the underlying structure model for this approach is less accurate than the present calculations and we do not include their numerical values in Table VI. The overall level of agreement between the Hylleraas and HFCP calculations is very impressive when it is considered that there are significant numerical cancellations in the calculation of α_1 that lead to a small value.

C. Effective potential for beryllium Rydberg state

Recently there have been a number of investigations of ion polarizabilities based on the interpretation of resonant excitation stark ionization spectroscopy (RESIS) [12,14–16]. The energy splitting of adjacent Rydberg levels with $\Delta L=1$ is used to determine the parent ion polarizabilities. One recent finding has been an increased appreciation of the importance of nonadiabatic and higher order polarizability terms proportional to $\mathbf{r}^{-7}$ and $\mathbf{r}^{-8}$ in the interpretation of the RESIS spectra.

Table VII summarizes all the parameters necessary to define the polarization series given by Eq. (7) for the Be$^+$ ion ground state. The data are presented since the neutral beryllium series represents an ideal system upon which to validate the underlying assumptions used in the analysis of the RESIS experiment. The nonadiabatic effects are strong [the nonadiabatic dipole polarizability of $\beta_1=-81.78175(1)$ dominates the quadrupole polarizability of $\alpha_2=53.7659(2)$ in the evaluation of $A_6=-218.4622(1)$] and all the "Hylleraas" polarizabilities listed in Table VII would have an overall level of precision better than 0.1%. Although no experiment has been

TABLE VI. Comparisons of the static polarizabilities and hyperpolarizabilities (in atomic units) for the $2\,^2S$ and $2\,^2P$ states of Be$^+$ ion.

	$2\,^2S$ state			
Method	α_1	α_2	α_3	γ_0
Coulomb approximation [17]	24.77			
Variation-perturbation Hylleraas CI [18]	24.5			
Asymptotic correct wave function [19]	24.91	53.01	465.7	
Variation-perturbation FCCI [20,21]	24.495	53.774(24)	465.79(11)	
HFCP	24.493	53.760	465.77	−11511
Hylleraas	24.4966(1)	53.7659(2)	465.7621(1)	−11521.30(3)

	2^2P state					
Method	α_1	α_1^T	α_2	α_3	γ_0	γ_2
HFCP	2.028	5.835	62.313	1208.8	10996	−7450.4
Hylleraas	2.02476(1)	5.856012(1)	62.2840(1)	1207.812(2)	10913.57(1)	−7373.61(5)

TABLE VII. The polarizability parameters and coefficients A_n of the polarization potential Eq. (7).

Method	α_1	β_1	α_2	β_2	α_3	δ_1	η	ϵ
Hylleraas	24.4966(1)	81.78175(1)	53.7659(2)	58.1169(1)	465.7621(1)	279.16401(2)	917.569(1)	1043.27(1)
HFCP	24.494	81.751	53.760	58.106	465.77	278.94	917.37	1038.7

	A_4	A_6	A_7	A_8	A_{8L}
Hylleraas	12.24830(5)	−218.4622(1)	−905.445(2)	9366.857(1)	1004.99051(8)
HFCP	12.247	−218.37	−904.99	9357.2	1004.2

done, a RESIS experiment upon neutral beryllium would provide a stringent test on the ability of an analysis based on Eq. (7) to extract polarizabilities from a typical RESIS spectrum.

D. Long-range dispersion coefficients

Tables VIII and IX list the long-range dispersion coefficients for the Be$^+$ ion interacting with the H, He, and Li atoms. Table VIII lists dispersion coefficients when both atoms or ions are in their ground states. Table IX gives dispersion coefficients when one of the systems in an excited state. All of the dispersion coefficients have been calculated independently using the Hylleraas and HFCP wave functions. Besides the wave functions, the procedures used to combine the lists of matrix elements were completely independent. As far as we know, the data listed in Tables VIII and IX are the only dispersion coefficients published for these systems.

The level of agreement between the two sets of C_n values is generally excellent. For example, the largest difference between any of the dispersion constants listed in Table VIII is only 0.06%, occurring for the Be$^+$(2 ^2S)-Li(2 ^2S) value of C_8.

The high level of agreement also occurs for the C_n values listed in Table IX, the only case of a greater than 1% difference occurring for the Be$^+$(2 ^2P)-Li(2 ^2S) dimer. In this case, the roughly 3% disagreement occurs as a result of the previously mentioned cancellations in the oscillator strength sum for the Be$^+$(2 ^2P) polarizability. The net effect of the cancellations is a reduction in the overall size of the dispersion constants by a factor of about 100. For example, the first term ($\lambda=0$) of Eq. (52) of Tang *et al.* [26] was −115.545 while the second term ($\lambda=2$) was 117.3969.

We do not list dispersion coefficients for the state combinations that allow Penning or associative ionization (this occurs when the excitation energy of one atom is sufficient to cause ionization in the other atom). When this is possible, there is a singularity in the energy denominator of the oscillator strength sum rules which makes it problematic to achieve convergence.

All the values in Table VIII and IX provide an important benchmark for the accurate determination of the interaction potentials between Be$^+$ ion and the H, He, or Li atoms. The

TABLE VIII. The long-range dispersion coefficients C_6 and C_8 for a ground state Be$^+$ ion interacting with a H, He, and Li atom. The first row for each system came from Hylleraas wave functions while the second row were computed with HFCP wave functions.

System	C_6	C_8
Be$^+$(2 ^2S)-H(1 ^2S)	18.8314(1)	371.675(5)
	18.829	371.62
Be$^+$(2 ^2S)-He(1 ^1S)	6.9811(1)	120.425(3)
	6.979	120.44
Be$^+$(2 ^2S)-He(2 ^1S)	621.577(2)	41371.9(1)
	621.52	41370
Be$^+$(2 ^2S)-He(2 ^3S)	400.289(3)	19753.9(2)
	400.26	19753
Be$^+$(2 ^2S)-Li(2 ^2S)	286.75(1)	11991.1(2)
	286.82	11998

TABLE IX. The long-range dispersion coefficients C_6, and C_8 for a Be$^+$ ion interacting with a H, He, and Li atom for the atomic states with a combined angular momentum of $L=1$. The M_b column denotes the total magnetic quantum number of the system. The first row for each system came from Hylleraas wave functions while the second row were computed with HFCP wave functions.

System	M_b	C_6	C_8
Be$^+$(2 ^2P)-H(1 ^2S)	0	38.53656(1)	1291.81(1)
	0	38.571	1292.7
Be$^+$(2 ^2P)-H(1 ^2S)	±1	17.12124(1)	172.578(1)
	±1	17.128	172.67
Be$^+$(2 ^2P)-He(1 ^1S)	0	11.64784(1)	438.3026(6)
	0	11.660	438.63
Be$^+$(2 ^2P)-He(1 ^1S)	±1	6.028208(7)	34.0606(3)
	±1	6.030	34.113
Be$^+$(2 ^2S)-He(2 ^3P)	0	791.311(4)	93960.4(9)
	0	791.52	93960
Be$^+$(2 ^2S)-He(2 ^3P)	±1	373.997(3)	3547.53(8)
	±1	374.25	3553.1
Be$^+$(2 ^2P)-Li(2 ^2S)	0	−326.06(8)	$-3.613643(6)\times 10^5$
	0	−325.74	-3.52050×10^5
Be$^+$(2 ^2P)-Li(2 ^2S)	±1	2.32(4)	$-1.214626(3)\times 10^5$
	±1	2.3964	-1.1836×10^5
Be$^+$(2 ^2S)-Li(2 ^2P)	0	925.279(2)	$1.043315(3)\times 10^5$
	0	925.49	1.0438×10^5
Be$^+$(2 ^2S)-Li(2 ^2P)	±1	420.470(1)	3804.79(4)
	±1	420.53	3806.7

BeH^+ ion is one of the few molecular ions [3] for which a potential curve could be computed with an explicitly correlated wave function. Hence the present values for the Be^+-H long-range interaction could be used to help construct a very accurate global potential surface for this system.

IV. CONCLUSION

Fully correlated Hylleraas variational wave functions have been used to determine definitive values for the oscillator strengths, polarizabilities and hyperpolarizabilities for the Be^+ ion $2\ ^2S$ ground state and the $2\ ^2P$ excited state. The Hylleraas results for the polarizabilities of the $2\ ^2S$ state improve the accuracy of previous values by more than one order of magnitude. Complementary calculations using a semi-empirical method have also been done. The high level of agreement between the two calculations at the 0.1% level of precision attests to the utility of carefully formulated effective potential approaches, which can give good descriptions of atomic structure with low computational expense.

The long-range dispersion coefficients for the Be^+ ion interacting with a H, a He, or a Li atom have been evaluated. The polarizabilities and dispersion coefficients provide reliable references for the description of ion-atom collisions involving Be^+ ion and also for high precision calculations of the potential curves between the Be^+ ion and atoms such as H, He, or Li.

In addition, all the parameters of the effective polarization potential for the Be^+ ion up to the $\mathbf{r}^{-8}$ term have been obtained. These parameters are extremely useful in the description of high-L Rydberg states of beryllium, and could be used in future experiments to determine the ionization potential of beryllium and also to describe the fine structure of beryllium atom Rydberg series. Furthermore, the present calculations lay the foundation for the further investigations of relativistic and QED effects on the polarizabilities and other properties of the Be^+ ion.

ACKNOWLEDGMENTS

This work was supported by NNSF of China under Grant No. 10674154 and by the National Basic Research Program of China under Grant No. 2005CB724508. Z.-C.Y. was supported by NSERC of Canada and by the computing facilities of ACEnet, SHARCnet, WestGrid, and in Part by the CAS/SAFEA International Partnership Program for Creative Research Teams. J.F.B was supported in part by the U.S. NSF through a grant for the Institute of Theoretical Atomic, Molecular and Optical Physics at Harvard University and Smithsonian Astrophysical Observatory. J.M. and J.Y.Z would like to thank the Wuhan Institute of Physics and Mathematics for its hospitality during their visits.

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