Research Article

Energies, Fine Structures, and Hyperfine Structures of the $1s^22snp \, ^3P \, (n = 2–4)$ States for the Beryllium Atom

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Energies and wave functions of the $1s^22snp \, ^3P \, (n = 2–4)$ states for the beryllium atom are calculated with the full-core plus correlation wave functions. Fine structures and hyperfine structures are calculated with the first-order perturbation theory. For the $1f^22p \, ^3P$ state, the calculated energies, fine structure, and hyperfine structure parameters are in good agreement with the latest theoretical and experimental data in the literature; it is shown that atomic parameters of the low-lying excited states for the beryllium atom can be calculated accurately using this theoretical method. For the $1s^22snp \, ^3P \, (n = 3, 4)$ states, the present calculations may provide valuable reference data for future theoretical calculations and experimental measurements.

1. Introduction

In recent years, studies of energies, fine structures, and hyperfine structures of the low-lying excited states for the beryllium atom [1–10] have been of great interest to spectroscopists because there are many strong optical transitions suitable for spectral and hyperfine structure measurements. On the other hand, studies of the low-lying excited states for the beryllium atom play an important role in developing the excited state theory of multielectron atoms and better understanding the complicated correlation effects between electrons. The fine structure comes from the spin-orbit, spin-other-orbit, and spin-spin interactions. The hyperfine structure of atomic energy levels is caused by the interaction between the electrons and the electromagnetic multipole moments of the nucleus. The leading terms of this interaction are the magnetic dipole and electric-quadrupole moments. The fine and hyperfine structure is sensitive to the correlation effects among electrons. Experimentally, some properties of the atomic nucleus can be obtained by investigating the hyperfine structure of the atomic energy levels. The nuclear electric-quadrupole moment, which is difficult to measure directly with nuclear physics techniques, can be determined using the measured hyperfine structure and the accurate theoretical results.

The $1s^22s^2p \, ^3P$ state of the beryllium atom is of interest since it is the lowest excited state in which hyperfine effects can occur, and the ground state has no hyperfine splitting because it is $J = 0$. It is generally a very demanding task to calculate hyperfine structure accurately. Polarization of the closed shells in the $1s^2$ core, due to the Coulomb interaction with open shells, can have a large effect on the hyperfine structure. Up till now, the most sophisticated theoretical calculations of the hyperfine structure parameters for the $1s^22s^2p \, ^3P$ state of the Be atom have been carried out using linked-cluster many-body perturbation (LC MBPT) theory [5, 6], Hartree-Fock and CI allowing all SD excitations to correlation orbitals of Slater type by Beck and Nicolaides [7], as well as multiconfiguration Hartree-Fock (MCHF) method [8, 9]. Experimentally, the magnetic dipole and electric-quadrupole hyperfine constants have been determined very accurately with the atomic-beam magnetic-resonance technique [10] for the $1s^22s^2p \, ^3P$ state in beryllium. To the best of our knowledge, few results on energies, fine structures, and hyperfine structures have been investigated for the $1s^22snp \, ^3P \, (n \geq 3)$ states of the beryllium atom due to the restriction of resolution from experiments and the numerical unsteadiness in theoretical calculations.

An elegant and complete variation approach, namely, the full core plus correlation (FCPC) method, has been developed by Chung [11, 12]. This method has been successfully applied to three- and four-electron systems, with the $1s^2$ core. Many elaborate calculations, especially for
the dipole polarizabilities [13], quadrupole and octupole polarizabilities [14], and total atomic scattering factors [15], show that FCPC wave functions have a reasonable behavior over the whole configuration space for three-electron systems. This method has also been used to calculate the hyperfine structure of the $1s^2n^2S$ and $1s^2np^2P$ states ($n = 2–5$) for the lithium isoelectronic sequence; the results are in good agreement with the Hylleraas calculations and with the experiment data [16]. As is well known, theoretical calculations of the hyperfine structure parameters depend sensitively on the behavior of the wave function in the proximity of the nucleus. In addition, core polarization effects for the low $l$ states need to be included in the nonrelativistic wave function. It would be interesting to find out whether the FCPC wave function can also be successful for calculating hyperfine structure parameters of low-lying excited states for the beryllium atom and provide more reliable theoretical data to stimulate further experimental measurements.

2. Theory

According to the FCPC method [11, 12], the wave function for the four-electron $1s^22snp^3P$ state can be written as

$$\Psi(1, 2, 3, 4) = A \Phi_{1s^2}(1, 2)\Phi_{2snp}(3, 4) + \sum C_i\Phi_{n(i), l(i)}(1, 2, 3, 4),$$

where $A$ is an antisymmetrization operator. $\Phi_{1s^2}$ is a predetermined $1s^2$-core wave function which is represented by a CI basis set,

$$\Phi_{1s^2}(1, 2) = A \sum C_{knl}r_1^kr_2^l \exp(-\beta r_1 - \rho r_2) Y_l(1, 2)\chi(1, 2),$$

the angular part is

$$Y_l(1, 2) = \sum m \langle l, m, l, -m | 0, 0 \rangle Y_l(m)(\theta_1, \varphi_1) Y_{l-m}(\theta_2, \varphi_2).$$

$\chi(1, 2)$ is a two-electron singlet spin function. The linear and nonlinear parameters in (2) are determined by optimizing the energy of the two-electron core. The factor $\Phi_{2snp}(3, 4)$ represents the wave function of the two outer electrons which is given by

$$\Phi_{2snp}(3, 4) = A \sum_{k, n, l} d_{knl}r_3^kr_4^l \exp(-\lambda r_3 - \eta r_4) Y_l(3, 4)\chi(3, 4),$$

the angular part is

$$Y_l(3, 4) = \sum_m \langle l, m, l + 1, -m | 0, 0 \rangle Y_l(m)(\theta_3, \varphi_3) Y_{l+1-m}(\theta_4, \varphi_4).$$

The latter wave function of (1) describes the core relaxation and the intrashell electron correlation in the four-electron system. It is given by

$$\Phi_{n(i), l(i)}(1, 2, 3, 4) = \varphi_{n(i), l(i)}(R)Y_{LM}^{l(i)}(\Omega)\chi_{SS},$$

where

$$\varphi_{n(i), l(i)}(R) = \prod_{j=1}^4 n_j^{l_j} \exp(-\alpha_j r_j).$$

A different set of $\alpha_j$ is used for each $l(i)$. The angular part is

$$Y_{LM}^{l(i)}(\Omega) = \sum_{m_j} \langle l_1l_2m_1m_2 | l_12m_1 \rangle \times \langle l_12m_1m_2 | l_123m_1m_3 \rangle \times \langle l_123m_1m_3m_4 | l_1234m_1m_3m_4 \rangle Y_{j,m_j}^{l(i)}(\Omega_{j}).$$

To simplify notation, this angular function is simply denoted as

$$l(i) = [(l_1, l_2)l_12, l_3]l_123, l_4,$$

with the understanding that $l_123$ and $l_4$ couple into $L$, the total orbital angular momentum. There are three possible spin functions for the $1s^22snp^3P$ state, namely,

$$\chi_1 = [(s_1, s_2)0, s_3] \frac{1}{2}, s_4,$$

$$\chi_2 = [(s_1, s_2)1, s_3] \frac{1}{2}, s_4,$$

$$\chi_3 = [(s_1, s_2)1, s_3] \frac{3}{2}, s_4.$$

For the radial basis functions of each angular-spin component, a set of linear and nonlinear parameters is chosen. These parameters are determined in the energy optimization process. For each set of $l_1$, $l_2$, $l_3$, and $l_4$, we try all possible $l(i)$ and $\chi$ and keep the ones which make significant contribution to the energy in (1).

The fine structure perturbation operators [1, 2] are given by

$$\hat{H}_{FS} = \hat{H}_{so} + \hat{H}_{soo} + \hat{H}_{aa},$$

where

$$\hat{H}_{so} = \sum_{l} \hat{H}_{so}^{l},$$

$$\hat{H}_{so}^{l} = \sum_{m} \langle l, m, l, -m | 0, 0 \rangle Y_l(m)(\theta_1, \varphi_1) Y_{l-m}(\theta_2, \varphi_2).$$

$$\hat{H}_{soo} = \sum_{l} \sum_{m} \langle l, m, l, -m | 0, 0 \rangle Y_l(m)(\theta_1, \varphi_1) Y_{l-m}(\theta_2, \varphi_2) Y_l(m)(\theta_3, \varphi_3) Y_{l-m}(\theta_4, \varphi_4).$$

$$\hat{H}_{aa} = \sum_{l} \sum_{m} \langle l, m, l, -m | 0, 0 \rangle Y_l(m)(\theta_1, \varphi_1) Y_{l-m}(\theta_2, \varphi_2) Y_l(m)(\theta_3, \varphi_3) Y_{l-m}(\theta_4, \varphi_4).$$
where the spin-orbit, spin-other-orbit, and spin-spin operators are
\[
\hat{H}_{SO} = \frac{Z}{2e^2} \sum_{i=1}^{4} \frac{-l_i \cdot \vec{s}_i}{r_i^3},
\]
\[
\hat{H}_{SOO} = -\frac{1}{2e^2} \sum_{i,j=1, i \neq j}^{4} \left( \frac{1}{r_{ij}} \right) \left( \vec{s}_i \cdot \vec{r}_j \right) \cdot \left( \vec{s}_j \cdot \vec{r}_i \right) / r_{ij}^3\right],
\]
\[
\hat{H}_{SS} = \frac{1}{c^2} \sum_{i,j=1}^{4} \frac{1}{r_{ij}^3} \left[ \vec{s}_i \cdot \vec{s}_j - \frac{3}{2} \left( \vec{s}_i \cdot \vec{r}_j \right) \left( \vec{s}_j \cdot \vec{r}_i \right) / r_{ij}^3 \right].
\]

To calculate the fine structure splitting, the LSJ coupling scheme is used:
\[
\Psi_{LsJz} = \sum_{\mu \lambda \sigma} (LSM \mu \lambda \sigma \sigma | J \lambda \sigma) \Phi_{LMS \mu \lambda \sigma}.
\] (13)

The fine structure energy levels are calculated by first-order perturbation theory
\[
(\Delta E_{FS})_J = \langle \Phi_{LsJz} | \hat{H}_{SO} + \hat{H}_{SOO} + \hat{H}_{SS} | \Phi_{LsJz} \rangle.
\] (14)

For an \(N\)-electron system, the hyperfine interaction Hamiltonian can be represented as follows [17, 18]:
\[
\hat{H}_{HFS} = \sum_{k=1}^{N} T^{(k)} \cdot M^{(k)},
\] (15)

where \(T^{(k)}\) and \(M^{(k)}\) are spherical tensor operators of rank \(k\) in the electronic and nuclear spaces, respectively. The \(k = 1\) term represents the magnetic-dipole interaction between the magnetic field generated by the electrons and nuclear magnetic dipole moments, and the \(k = 2\) term the electric quadrupole interaction between the electric-field gradient from the electrons and the nonspherical charge distribution of the nucleus. The contributions from higher-order terms are much smaller and can often be neglected.

In the nonrelativistic framework, the electronic tensor operators, in atomic units, can be written as
\[
T^{(1)} = \frac{\alpha^2}{2} \sum_{i=1}^{4} \left[ 2g_i r_i^{-3} l_i^{(1)} - \sqrt{10} g_i \{ s_i^{(1)} C_i^{(2)} \} r_i^{-3} \right] + \frac{8\pi}{3} g_i s_i^{(1)} \delta(r_i)\right]
\] (16)
\[
T^{(2)} = -\sum_{i=1}^{4} r_i^{-3} C_i^{(2)},
\]

where \(g_i = (1 - m_i/M)\) is the orbital electron g factor, and \(g_i = 2.0023193\) is the electron spin g factor. \(M\) is the nuclear mass. The tensor \(C_i^{(2)}\) is connected to the spherical harmonics \(Y_{lm}(i)\) by
\[
C_i^{(2)} = \sqrt{\frac{4\pi}{2l+1}} Y_{lm}.
\] (17)

The hyperfine interaction couples the electronic angular momenta \(J\) and the nuclear angular momenta \(I\) to a total angular momentum \(F = I + J\). The uncoupling and coupling hyperfine constants are defined in atomic units as [17, 18]:
\[
a_c = \left\langle \gamma L M_L M_S \right| \sum_{i=1}^{N} 8\pi \delta^2(r_i) s_0(i) \right| \gamma L M_L M_S \rightangle
\] (Fermi contact),
\[
a_{SD} = \left\langle \gamma L M_L M_S \sum_{i=1}^{N} 2C_0^{(2)}(i)s_0(i)r_i^{-3} \right| \gamma L M_L M_S \rightangle
\] (Spin dipolar),
\[
a_l = \left\langle \gamma L M_L M_S \left| \sum_{i=1}^{N} l_0(i)r_i^{-3} \right| \gamma L M_L M_S \rightangle
\] (orbital),
\[
b_q = \left\langle \gamma L M_L M_S \left| \sum_{i=1}^{N} 2C_0^{(2)}(i)s_0(i)r_i^{-3} \right| \gamma L M_L M_S \rightangle
\] (electric quadrupole),
\[
A_J = \frac{\mu_I}{1} \left[ \frac{1}{(J + 1)(2J + 1)} \right]^{1/2} \left\langle yJ \left| T^{(1)} \right| yJ \right\rangle,
\]
\[
A_{J-1} = \frac{\mu_I}{1} \left[ \frac{1}{(J - 1)(2J - 1)} \right]^{1/2} \left\langle yJ - 1 \left| T^{(1)} \right| yJ \right\rangle,
\]
\[
B_J = 2Q \left[ \frac{2J - 1}{(2J + 1)(2J + 2)(2J + 3)} \right]^{1/2} \left\langle yJ \left| T^{(2)} \right| yJ \right\rangle,
\]
(18)

where \(M_L = L\) and \(M_S = S\). In these expressions, \(\mu_I\) is the nuclear magnetic moment and \(Q\) is the nuclear electric quadrupole moment. \(l\) is the nuclear spin, and \(J\) is the atomic electronic angular momentum.

3. Results and Discussions

In order to achieve accurate calculation results for various properties of the low-lying excited states for the beryllium atom, the choice of basis function with sufficiently high quality is critical and it is our major concern. The seven \(l\) components \((0,0), (1,1), (2,2), (3,3), (4,4), (5,5), (6,6)\) altogether 159 terms are used for the \(1s^2\) core. The \(\Phi_{2snp}\) in (1) has four angular components, \(l\) is summed from 0 to 3 with the angular components \(0,1, 2, 3\), and \(3, 4, 5, 6\), and the number of terms in \(\Phi_{2snp}\) ranges from 36 to 15. Most of the other correlation effects are included in (6), which accounts for the intershell as well as the intrashell correlations. Many relevant angular and spin couplings are important for the energy, these basis functions are tried to include in \(\Phi_{n(i,j)\lambda}\) \((1, 2, 3, 4)\) with significant energy contribution. For each set of orbital angular momenta \(l_1, l_2, l_3, l_4\), there could be several ways to couple this set into the desired total orbital angular momentum. In this work,
for $1s^22snp^3P$ states, the important angular series $(l_1, l_2, l_3, l_4)$ are $(0, 0, l, (l+1))$, $(0, 1, l, l)$, $(l, l, 0, 1)$, and so forth. In both cases, the value of $l$ is from 0 to 6, as the energy contribution from set with $l > 6$ is small and negligible. In order to get the high-quality wave function, the number of angular-spin components in the $\Phi_{n(\ell_{l1}, \ell_{l2})}$ wave functions ranges from 15 to 66, and the number of terms in the $\Phi_{n(\ell_{l1}, \ell_{l2})}$ of (6) is about 790. The linear and nonlinear parameters are individually optimized in the energy minimization process. Using the Rayleigh-Ritz variational method, the basic wave function $\Psi$ and the corresponding eigenvalue $E$ are determined.

Nonrelativistic energies of the $1s^22snp^3P$ ($n = 2–4$) states for the beryllium atom are given in Table 1. As Table 1 shows, for the $1s^22snp$ ($n = 2, 3$) $^3P$ states, the nonrelativistic energies in this work are lower and better than those of Hibbert and Weiss [1, 2], the improvement ranging from 0.0479 a.u. to 0.0473 a.u. Hibbert and Weiss reported a set of large-scale configuration interaction (CI) calculations for the $1s^22snp$ ($n = 2, 3$) $^3P$ states, which can give an accurate approximation for each state, but it may tend to obscure the global picture of the spectrum which is so transparent in the other approach. The work of Hibbert and of Weiss did not include any intrashell correlation in the 1s shell, as the calculations were of transitions in the outer subshells. The correlation energy of the 1s shell is almost independent of the nuclear charge and also of the number of additional electrons outside the 1s shell. For Be, it is about 0.0457 a.u. and this accounts for the main difference between earlier work and the present; more accurate results are presented in Table 1. Of course, for the calculation of hyperfine parameters, correlation within the 1s shell is crucial in obtaining accurate hyperfine parameters, and this has been achieved in the present work. For the $1s^22sp^3P$ state, the present calculation from the FCPC method is also lower than the result of Weiss [2].

If including the effects of the spin-orbit, spin–other-orbit, and spin-spin interactions, the energies of the fine structure resolved $J$ levels are obtained. In this work, the fine structure splittings of the triplet states are calculated with the $H_{so}$, $H_{soo}$, and $H_{so}$ operators using the first-order perturbation theory. Table 2 gives the fine-structure splittings of the $1s^22snp^3P$ ($n = 2–4$) states for the beryllium atom. The experimental Be $2s^2p^3P$ splitting is 2.35 ($J = 2 \rightarrow 1$) and 0.64 ($J = 1 \rightarrow 0$) cm$^{-1}$ [3]. They agree with our prediction 2.36 and 0.64 cm$^{-1}$. Although many theoretical studies have been done on the Be excited systems, the published theoretical fine structure results are scarce. One exception is Laughlin, Constantinides, and Victor [4]. They use a model potential calculation and predict the splittings to be 2.53 and 0.71 cm$^{-1}$ for the $1s^22s2p^3P_f$ state, which should be considered as quite good in view of the simplicity in their computation and fall in experimental uncertainties. Present calculations for this state are more accurate due to correlation effect well described in this method. For the experiment, the splitting of $1s^22s3p^3P_J (J = 1, 0)$ is not resolved. But the splitting from the $J = 2$ state to the $J = 1, 0$ is determined to be 0.37 cm$^{-1}$. In this work, the calculated splittings are 0.35 ($J = 2 \rightarrow 1$) and 0.092 ($J = 1 \rightarrow 0$) cm$^{-1}$. This implies that the predicted splitting from $J = 2$ to the center of gravity of $J = 1$ and 0 should be 0.373 cm$^{-1}$. It agrees with the experiment. The good agreement with experiment could be used as the indication of the accuracy of the wave function constructed here. For the $1s^22s4p^3P_f$ state, our calculated splittings are hoped to offer reference for further experimental measurements.

The hyperfine structure parameters of the $1s^22snp^3P (n = 2–4)$ states for the beryllium atom are calculated in this work: Fermi contact $a_c$, the spin dipolar $a_{SD}$, the orbital $a_l$, and the electric quadrupole $b_q$. In the present calculation, $Q = 0.0530b, \mu_I = -1.177492 \mu m, I = 1.5$ for Be are taken from [19]. The hyperfine interaction in the $1s^22s2p^3P$ state for the beryllium atom is of interest since it is the lowest excited state in which hyperfine effects can occur, which has

### Table 1: Nonrelativistic energies of the $1s^22snp^3P$ ($n = 2–4$) states for the beryllium atom (in a.u.).

<table>
<thead>
<tr>
<th>$n$</th>
<th>This work</th>
<th>Hibbert$^a$</th>
<th>Weiss$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>14.56637</td>
<td>14.5184</td>
<td>14.51844</td>
</tr>
<tr>
<td>4</td>
<td>14.36248</td>
<td></td>
<td>14.31530</td>
</tr>
</tbody>
</table>

$^a$Reference [1].

$^b$Reference [2].

### Table 2: Fine structure splittings $\nu_{1f}$ of the $1s^22snp^3P_f$ ($n = 2–4$) states for the beryllium atom (in cm$^{-1}$).

<table>
<thead>
<tr>
<th>$n$</th>
<th>$1s^22s2p^3P_f$</th>
<th>$1s^22s3p^3P_f$</th>
<th>$1s^22s4p^3P_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.36</td>
<td>0.35</td>
<td>0.13</td>
</tr>
<tr>
<td>3</td>
<td>2.35 (2)</td>
<td>0.092</td>
<td>0.034</td>
</tr>
<tr>
<td>4</td>
<td>0.64 (1)</td>
<td>0.71</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Reference [3].

$^b$Reference [4].
been studied over the past four decades [5–10]. Table 3 gives the hyperfine structure parameters of the $1s^22s2p^3P$ state for the beryllium atom through the FCPC wave function to compare with data in the literature. As can be seen from Table 3, the present results for hyperfine structure parameters are better than the earlier theoretical results [5–7] in whole. The present calculations also agree with the results by FE MCHF (finite-element multiconfiguration Hartree-Fock) method [8] to two significant figures. The calculated Fermi contact term in this work differs from the results from the latest calculation through MCHF method [9] by only 0.07%, and the differences for the other terms are on the order of a few parts in a thousand. This means that the wave function used in the present work is reasonable and accurate in the full configuration space. The hyperfine coupling constants $A_1$ are also listed in Table 3 to compare with results from other calculations and experiments. Our calculated hyperfine coupling constants agree perfectly with the experimental value [10] to four significant figures. That is also true for the MCHF calculation of [9]. It is shown that hyperfine structure parameters of the low-lying excited states for the beryllium atom can be calculated accurately using the present FCPC wave function. For the $1s^22snp^3P$ ($n = 3, 4$) states, to the best of our knowledge, there is no report on hyperfine structure parameters in the literature. The present predictions for the hyperfine structure parameters and coupling constants are listed in Table 4, which may provide valuable reference data for other theoretical calculations and experimental measurements.

### 4. Summary

In this work, energies, fine-structure splittings, and hyperfine structure parameters of the $1s^22snp^3P$ ($n = 2–4$) states for the beryllium atom are calculated with the FCPC wave functions. The obtained nonrelativistic energies are much lower than the previous published theoretical values. The calculated fine structure splittings are in good agreement with experiment. For the $1s^22s2p^3P$ state, the calculated hyperfine structure parameters are in good agreement with the latest theoretical and experimental data in the literature; it is shown that hyperfine constants of the low-lying excited states for the beryllium atom can be calculated accurately using this kind of wave function. For other states, the present predicted hyperfine structure parameters may provide valuable reference data for future theoretical calculations and experimental measurements.

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