

# Quantum defects of nonpenetrating Rydberg states of the SO molecule in adiabatic and nonadiabatic regions of the spectrum

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This paper is dedicated to the implementation of a generalized approach for calculating quantum defects in high Rydberg states of polar molecules with an account for the dipole moment of the molecular core and  $l$  uncoupling of the Rydberg electron. Adiabatic (Born-Oppenheimer) and nonadiabatic (inverse Born-Oppenheimer) regions of the spectrum are considered. The nonadiabatic case with a nonzero projection of the core momentum on the core axis is considered and is illustrated by the example of the SO molecule.

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## I. INTRODUCTION

Sulfur monoxide (SO) and its cation  $\text{SO}^+$  are of great interest for a number of chemical and astrophysical problems. In particular, they are observed in interstellar clouds and planetary atmospheres, including the atmosphere of Jupiter and Earth's troposphere where they are important intermediates in atmospheric chemical processes [1–12]. Therefore, high Rydberg spectra of SO and  $\text{SO}^+$  are of great interest for these applications. Unfortunately, traditional *ab initio* techniques are not effective for excited electron states even for such a simple molecule as SO, therefore, it is necessary to use other techniques based on the quantum-defect approach.

A general theoretical basis for the description of molecular Rydberg states was given by Seaton in classical papers, which were written in the 1960s [13,14]. Since then, it developed into a powerful multichannel quantum-defect theory (MQDT), which was applied first to nonpolar molecules [15–21]. Later, the MQDT technique was improved greatly and was applied to several polar molecules, such as NO [22], CaF [23–28], BaF [24,29–32], CaCl [33–35], etc. A consistent nonperturbative approach to include the effect of the long-range dipole potential of a polar core was built in the papers of Zon [36] and Watson [37]. Its variant for the strongly nonadiabatic conditions of the inverse Born-Oppenheimer (IBO) approximation was developed in Ref. [38]. It was extended further to take the complex structure of the core [39] and the effect of the core  $\omega$  doubling [40] into account. In combination with the Green's-function technique, it was used to develop a method for the calculation of the polarizability of the nonpolar [41] and polar molecules NO [42], LiH, NaH, CaF, and BF [43].

Nonpenetrating Rydberg states are responsible for the enormous lifetime enhancement of high Rydberg states, which is essential in zero electric kinetic energy and mass-analyzed threshold ionization techniques [44–46]. This effect is observed not only in atoms and simple molecules, but also in large polyatomic molecules [47].

At the same time, even small quantum defects of nonpenetrating Rydberg states are essential for the processes of near-threshold-field ionization because the value of the quantum

defect determines the adiabatic or diabatic mechanism of the ionization [44] and rotational autoionization [48]. It must be noted that an investigation of the Rydberg states recently have attracted the particular attention in relation to important scientific and technological applications (see, for instance, Refs. [49–54] and references therein).

In the present paper, we give a brief outline of the general classification for the nonpenetrating Rydberg states of the polar molecules in both BO and IBO regions, and as an example, we apply it to a specific polar molecule, namely, SO.

Atomic units are used throughout.

## II. MAIN FORMALISM

### A. BO approximation

Additional difficulties in describing Rydberg molecules as compared with Rydberg atoms stem from two circumstances: (i) the presence of vibrational and rotational spectra and (ii) the presence of a long-range dipole potential of the core. Indeed, quadrupole moments are characteristic of both molecules and atoms, and, in both cases, multipole moments of higher orders can be included in the short-range part of the potential. The effect of the atomic-core polarizability on quantum defects is considered in Ref. [55]. Effects involving the spin of the Rydberg electron are not considered in the present paper with the exception of the magnetic dipole-dipole interaction [Eq. (16) below].

We confine our consideration to nonpenetrating Rydberg states, i.e., the states with negligible penetration of the Rydberg electron into the molecular core. Estimations show that, for example, for  $\text{H}_2$  and CaF, the Rydberg states with  $l \geq 2$  and  $l \geq 3$ , respectively, can be considered as nonpenetrating ones (see, for example, Refs. [24,56]), and such a critical value of  $l$  also can be assumed for the majority of other diatomic molecules, including SO. In nonpenetrating states, the motion of the Rydberg electron is influenced mainly by the Coulomb and dipole parts of the core potential, which allows separation of the Rydberg electron wave function into the radial part and the angular one in the limits of BO and IBO approximations as presented below. In the intermediate region between BO and IBO, such separation is not possible, and the wave function should be found numerically.

In this section, we consider the problem of the influence of a dipole moment on the motion of a Rydberg electron in the

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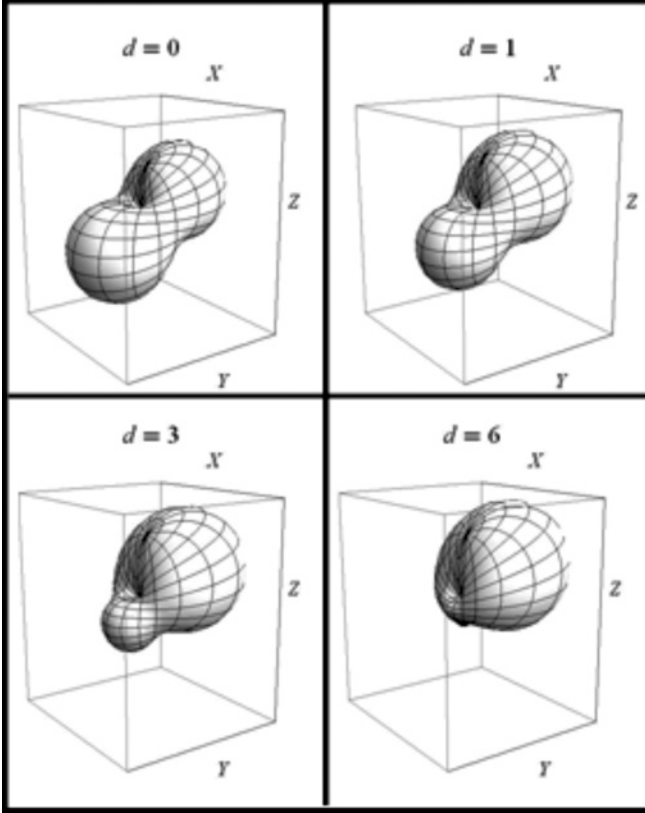


FIG. 1.  $|Z_{lk}^{IBO}|$  as a function of  $\theta, \varphi$  for  $\bar{s} = j = 5/2$ ,  $M_s = 3/2$ ,  $\omega = 1/2$ ,  $l = 1$ ,  $\Omega = \{\pi/2, \pi/2, \pi/2\}$ , and  $d = 0, 1, 3, 6$  a.u.

ordinary BO approximation. It takes place when the precession of the Rydberg electron orbit is more rapid than the rotation of the core and, hence, the angular momentum of the Rydberg electron strongly coupled to the core symmetry axis. It follows that this approximation takes place if the following inequality is valid [57]:

$$4Bj \ll \frac{|\mu|}{n^3} = |\Delta E_{QD}|. \quad (1)$$

Here,  $B$  is the rotational constant,  $j$  is the total momentum of the core,  $n$  is the principal quantum number of the Rydberg state,  $\mu$  is the quantum defect [i.e., the correction of the principal quantum number in the familiar Rydberg formula  $E_n = -\frac{1}{2}(n - \mu)^{-2}$ ], and  $\Delta E_{QD}$  is the energy shift due to the quantum defect.

In this approximation, the motion of the Rydberg electron can be considered in the molecular-core reference frame. We write the Schrödinger equation for the Rydberg electron in the form

$$H_0 \Psi = E \Psi, \quad (2)$$

$$H_0 = \frac{p^2}{2} + \frac{d}{r^2} \cos \theta - \frac{1}{r}. \quad (3)$$

Here,  $d$  is the dipole moment of the core,  $\theta$  is the angle between  $\mathbf{d}$  and  $\mathbf{r}$ , and  $p$  is the Rydberg electron momentum. We can separate variables in Eq. (2) and can seek the wave function in the form

$$\Psi(\mathbf{r}) = R(r)Z^{BO}(\theta, \varphi). \quad (4)$$

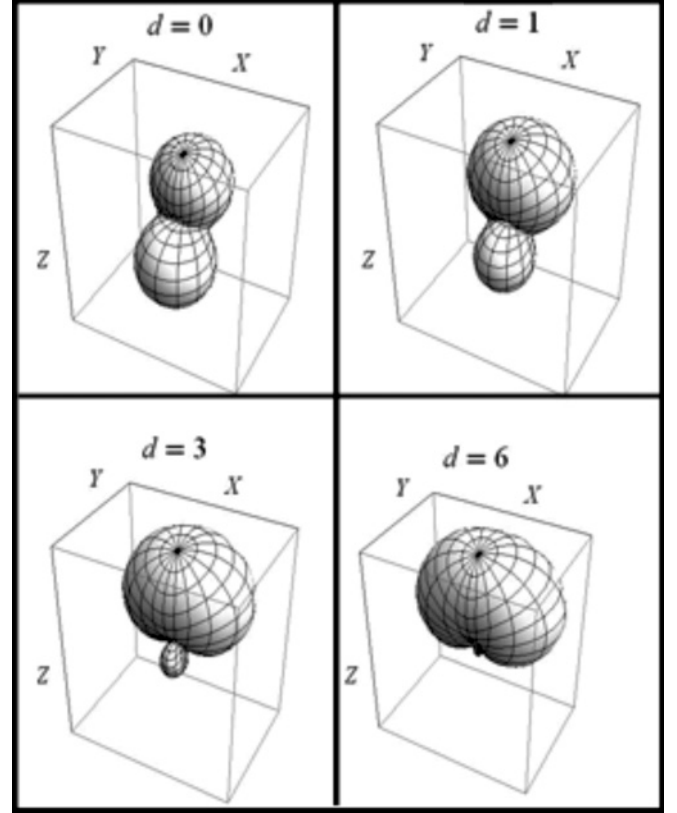


FIG. 2.  $|Z_{lk}^{IBO}|$  as a function of  $\theta, \varphi$  for  $\bar{s} = j = 5/2$ ,  $M_s = 3/2$ ,  $\omega = 1/2$ ,  $l = 1$ ,  $\Omega = \{\pi/2, \pi/4, \pi/2\}$ , and  $d = 0, 1, 3, 6$  a.u.

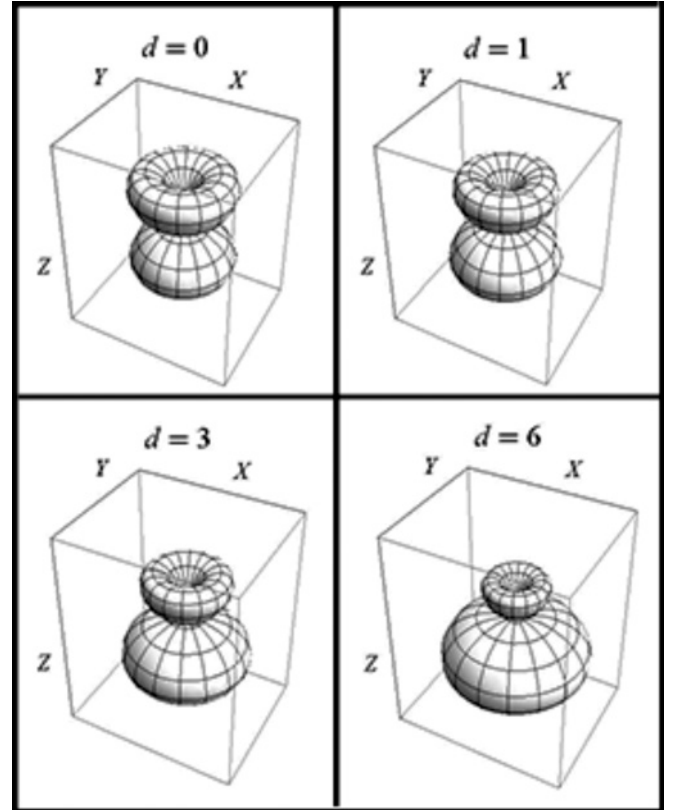


FIG. 3.  $|Z_{lk}^{IBO}|$  as a function of  $\theta, \varphi$  for  $\bar{s} = j = 5/2$ ,  $M_s = 3/2$ ,  $\omega = 1/2$ ,  $l = 2$ ,  $\Omega = \{0, 0, 0\}$ , and  $d = 0, 1, 3, 6$  a.u.

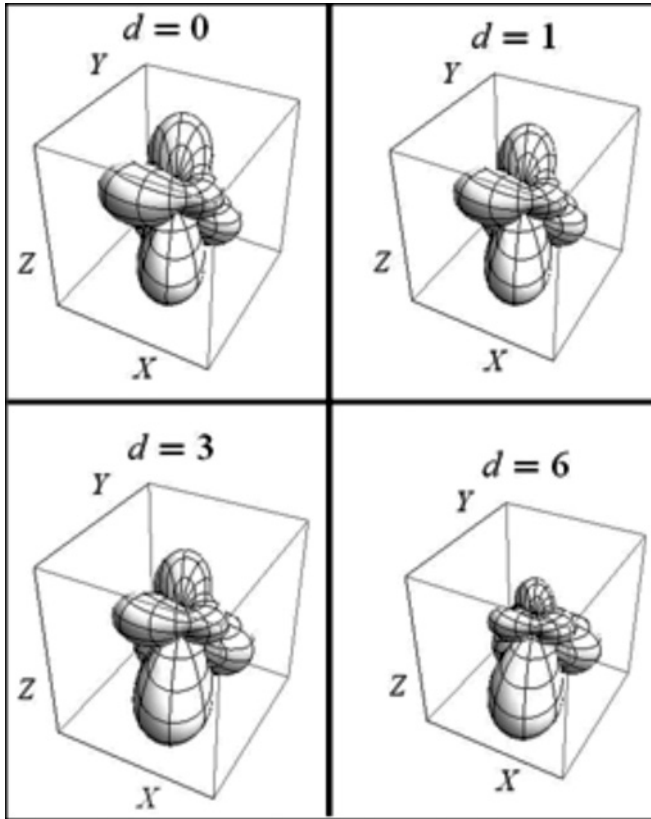


FIG. 4.  $|Z_{lk}^{\text{BO}}|$  as a function of  $\theta, \varphi$  for  $\bar{s} = j = 5/2$ ,  $M_{\bar{s}} = 3/2$ ,  $\omega = 1/2$ ,  $l = 2$ ,  $\Omega = \{0, \pi/2, 0\}$ , and  $d = 0, 1, 3, 6$  a.u.

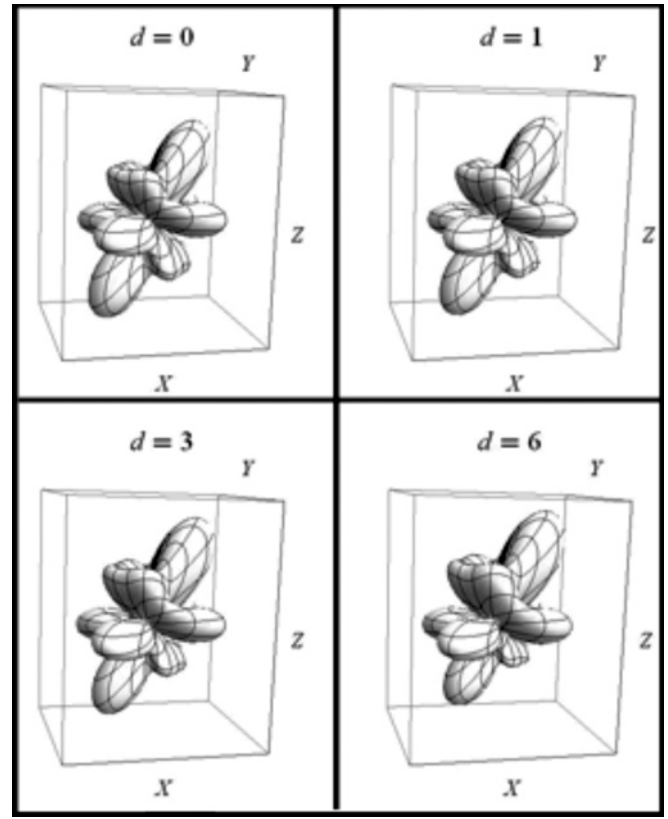


FIG. 6.  $|Z_{lk}^{\text{BO}}|$  as a function of  $\theta, \varphi$  for  $\bar{s} = j = 5/2$ ,  $M_{\bar{s}} = 3/2$ ,  $\omega = 1/2$ ,  $l = 3$ ,  $\Omega = \{0, \pi/2, 0\}$ , and  $d = 0, 1, 3, 6$  a.u.

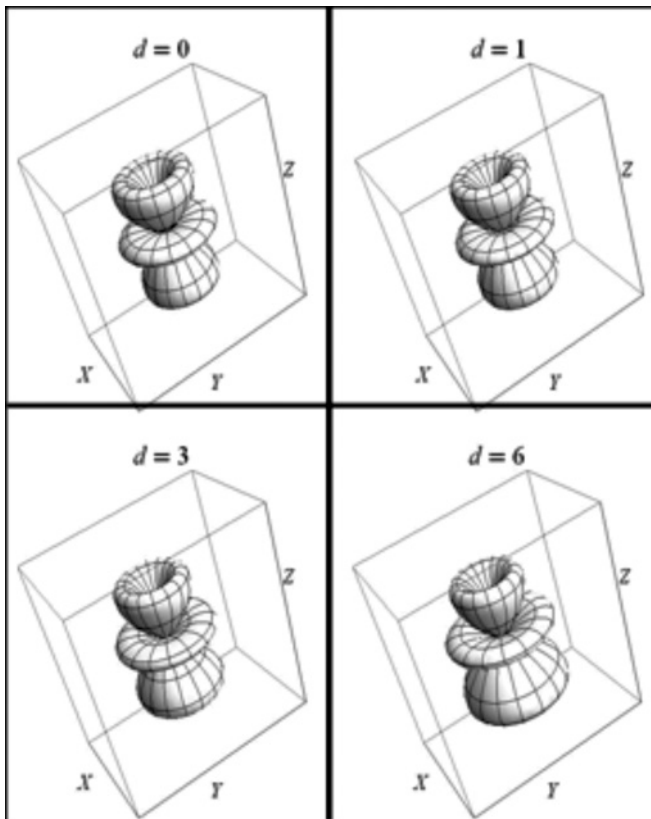


FIG. 5.  $|Z_{lk}^{\text{BO}}|$  as a function of  $\theta, \varphi$  for  $\bar{s} = j = 5/2$ ,  $M_{\bar{s}} = 3/2$ ,  $\omega = 1/2$ ,  $l = 3$ ,  $\Omega = \{0, 0, 0\}$ , and  $d = 0, 1, 3, 6$  a.u.

We call  $\Psi(\mathbf{r})$  the BO Coulomb-dipole function. Here, function  $Z^{\text{BO}}(\theta, \varphi)$  satisfies the equation,

$$\Delta_{\theta, \varphi} Z_{lm}^{\text{BO}} + 2d \cos \theta Z_{lm}^{\text{BO}} = \lambda^{(lm)} Z_{lm}^{\text{BO}}, \quad (5)$$

where  $\Delta_{\theta, \varphi}$  is the angular part of the Laplacian,  $m$  is the Rydberg electron's azimuthal quantum number (which is an integral of motion in the BO approximation, if the quantization axis is directed along the core-dipole moment direction),  $l$  is the index that enumerates different eigenfunctions corresponding to the same  $m$ , and parameter  $\lambda$  is the separation constant that must be found in the process of the solution. If  $d = 0$ , then obviously,  $\lambda^{(lm)} = l(l + 1)$  for all  $m$ , and  $Z_{lm}^{\text{BO}} = Y_{lm}(\theta, \varphi)$ ,

TABLE I. Quadrupole moment  $Q$ .

| Basis set  | Method          |                  |                  |                    |
|------------|-----------------|------------------|------------------|--------------------|
|            | HF <sup>a</sup> | MP2 <sup>b</sup> | MP4 <sup>c</sup> | B3LYP <sup>d</sup> |
| 6-311G     | 0.64            | 0.71             | 0.79             | 0.72               |
| 6-311 + G  | 0.67            | 0.70             | 0.77             | 0.77               |
| 6-311 + +G | 0.63            | 0.69             | 0.78             | 0.75               |

<sup>a</sup>HF denotes Hartree-Fock.

<sup>b</sup>MP2 denotes second-order Møller-Plesset.

<sup>c</sup>MP4 denotes fourth-order Møller-Plesset.

<sup>d</sup>B3LYP denotes the Becke three-parameter Lee-Yang-Parr hybrid functional.

TABLE II. Quantum defect  $\mu_d$  induced by the core-dipole moment for the BO region, Eq. (10).

| $m$ | $l$     |          |          |          |          |          |
|-----|---------|----------|----------|----------|----------|----------|
|     | 0       | 1        | 2        | 3        | 4        | 5        |
| 0   | -0.7334 | -0.10576 | -0.02385 | -0.00771 | -0.00357 | -0.01104 |
| 1   |         | 0.08036  | -0.01006 | -0.00573 | -0.00304 | -0.01060 |
| 2   |         |          | 0.02297  | 0.00011  | -0.00144 | -0.00928 |
| 3   |         |          |          | 0.00959  | 0.00120  | -0.00707 |
| 4   |         |          |          |          | 0.00487  | 0.00113  |
| 5   |         |          |          |          |          | 0.00281  |

where  $Y$  is the ordinary spherical harmonic. Oppositely, if  $d \neq 0$ , then  $Z_{lm}^{\text{BO}}$  can be sought in the form of expansion,

$$Z_{lm}^{\text{BO}}(d; \theta, \varphi) = \sum_{l'=|m|}^{\infty} a_{l'}^{(lm)} Y_{l'm}(\theta, \varphi), \quad (6)$$

where the coefficients  $a_{l'}^{(lm)}$  satisfy the relations,

$$2d \sum_{l''=l' \pm 1} \left( \frac{2l''+1}{2l'+1} \right)^{1/2} C_{l''0}^{l'0} C_{l''m}^{l'm} a_{l''}^{(lm)} = [\lambda^{(lm)} - l'(l'+1)] a_{l'}^{(lm)}. \quad (7)$$

Here,  $C$  are the Clebsch-Gordan coefficients. Thus, the constants  $\lambda^{(lm)}$  and the set of coefficients  $a_{l'}^{(lm)}$  can be found numerically as the eigenvalues and the eigenvectors, respectively, of the system (7). The values  $\lambda^{(lm)}$  can be expressed in terms of the effective angular momentum number,

$$\lambda^{(lm)} = \tilde{l}(\tilde{l}+1), \quad (8)$$

and reversely,

$$\tilde{l} = \sqrt{\lambda^{(lm)} + 1/4} - 1/2. \quad (9)$$

Then, the quantum defects induced by the core-dipole moment can be found as

$$\mu_d = l - \tilde{l} = l - \sqrt{\lambda^{(lm)} + 1/4} + 1/2. \quad (10)$$

The graphs for several functions  $Z_{lm}^{\text{BO}}$  are given in Ref. [58]. Corresponding results for the SO molecule are presented in Tables II, III, and VI and are discussed in Sec. III. The radial functions satisfy the equation,

$$\Delta_r R + 2 \left[ \frac{1}{r} + E \right] R - \frac{\lambda^{(lm)}}{r^2} R = 0, \quad (11)$$

TABLE III. Quantum defect  $\mu_Q$  for the BO region, Eq. (15).

| $m$ | $l$   |          |          |          |          |
|-----|-------|----------|----------|----------|----------|
|     | 1     | 2        | 3        | 4        | 5        |
| 0   | 0.1   | 0.01429  | 0.00476  | 0.00216  | 0.00117  |
| 1   | -0.05 | 0.00714  | 0.00357  | 0.00184  | 0.00105  |
| 2   |       | -0.01429 | 0        | 0.00087  | 0.00070  |
| 3   |       |          | -0.00595 | -0.00076 | 0.00012  |
| 4   |       |          |          | -0.00303 | -0.00070 |
| 5   |       |          |          |          | -0.00175 |

where  $\Delta_r$  is the radial part of the Laplacian. The solution of Eq. (11) essentially is the conventional radial Coulomb function with a modification of the familiar integer  $l$  on  $\tilde{l}$ ,

$$R_\nu(\lambda, r) = \frac{1}{\nu r} \left( \frac{n_r!}{\Gamma(n_r + \tilde{l} + 1)} \right)^{1/2} \left( \frac{2r}{\nu} \right)^{\tilde{l}+1} \exp\left(-\frac{r}{\nu}\right) \times L_{n_r}^{2\tilde{l}+1} \left( \frac{2r}{\nu} \right), \quad \nu = n_r + \tilde{l} + 1. \quad (12)$$

Here,  $n_r = 0, 1, \dots$  is the radial quantum number.

Additionally, one can take the quadrupole moment of the molecular core  $Q$  into account, including it as a small perturbation into the Hamiltonian,

$$H = H_0 + \sqrt{\frac{4\pi}{5}} \frac{Q}{r^3} Y_{20}(\theta, \varphi). \quad (13)$$

For small  $d, Q$ , one can derive the following asymptotical expressions for the corresponding contributions into the quantum defect for  $l > 0$  [24,25]:

$$\mu_d = -\frac{2[l(l+1) - 3m^2]}{l(l+1)(2l-1)(2l+1)(2l+3)} d^2, \quad (14)$$

$$\mu_Q = \frac{2[l(l+1) - 3m^2]}{l(l+1)(2l-1)(2l+1)(2l+3)} Q. \quad (15)$$

For  $l = 0$ ,  $\mu_d \approx -2d^2/3$  and  $\mu_Q = 0$ .

In a similar way, magnetic effects also can be taken into account. The magnetic dipole-dipole interaction between the core and the Rydberg electron is

$$H_M = \frac{\mu_B^2}{r^3} (\mathbf{L}^+ + 2\mathbf{S}^+) (\mathbf{L} + 2\mathbf{s}), \quad (16)$$

where  $\mu_B$  is the Bohr magneton,  $\mathbf{L}^+$ ,  $\mathbf{S}^+$ ,  $\mathbf{L}$ , and  $\mathbf{s}$  are the angular momentum and spin of the core and the Rydberg electron, respectively. However, the corresponding contribution into the quantum defect typically is several orders less than  $\mu_d$  and  $\mu_Q$  due to the smallness of  $\mu_B = e\hbar/(2mc) \simeq 1/274$  a.u.

## B. IBO approximation

IBO approximation takes place for high Rydberg states when the precession of the Rydberg electron orbit is slower than the rotation of the core and the angular momentum of the electron uncouples from the core axis [57],

$$4Bj \gg \frac{|\mu|}{n^3} = |\Delta E_{\text{QD}}|. \quad (17)$$

TABLE IV. Quantum defect  $\mu_d$  induced by the core-dipole moment for the IBO region, Eq. (22).

| $j$ | $\bar{s}$ | $l$      |           |           |           |           |         |
|-----|-----------|----------|-----------|-----------|-----------|-----------|---------|
|     |           | 0        | 1         | 2         | 3         | 4         | 5       |
| 1/2 | 1/2       | 0.400 36 | -0.078 00 |           |           |           |         |
|     | 3/2       |          | 0.044 05  | -0.025 91 |           |           |         |
|     | 5/2       |          |           | 0.017 73  | -0.012 60 |           |         |
| 3/2 | 1/2       |          | 0.001 79  | -0.001 07 |           |           |         |
|     | 3/2       | 0.055 80 | -0.011 77 | -0.002 15 | -0.000 92 |           |         |
|     | 5/2       |          | 0.007 52  | -0.001 88 | -0.001 05 | -0.000 64 |         |
| 5/2 | 1/2       |          |           | 0.000 13  | -0.000 09 |           |         |
|     | 3/2       |          | 0.001 38  | -0.000 35 | -0.000 19 | -0.000 12 |         |
|     | 5/2       | 0.0234   | -0.004 80 | -0.000 77 | -0.000 29 | -0.000 16 | -0.0001 |

We confine the consideration of the IBO approximation to the situation when the molecular core has a form of a symmetric top whose dipole moment is directed along the symmetry axis [38]. Let us write the Hamiltonian,

$$H_0 = H^+ + \frac{p^2}{2} - \frac{1}{r} + \frac{\mathbf{d}\mathbf{r}}{r^3}, \quad (18)$$

where

$$H^+ = B j^2 + (C - B) j_z^2 \quad (19)$$

is the rotational part of the Hamiltonian of the core,  $B$  and  $C$  are the rotational constants,  $j$  is the total momentum of the core, and  $j_z$  is the projection of this momentum on the symmetry axis. Here, we assume Hund's case (a) for the core (for other cases, see Refs. [39,57]).

Taking these circumstances into account, we search for the solution to the Schrödinger equation in the form

$$\Psi(\Omega, \mathbf{r}) = R(r) Z^{\text{IBO}}(\Omega; \theta, \varphi), \quad (20)$$

$$Z_{lk}^{\text{IBO}} = \sqrt{\frac{2j+1}{8\pi^2}} \sum_{l'} a_{l'}^{(lk)} \sum_{l_z} C_{jz l' l_z}^{\bar{s} M_{\bar{s}}} D_{j_z \omega}^{j*}(\Omega) Y_{l' l_z}(\theta, \varphi). \quad (21)$$

We call  $\Psi(\Omega, \mathbf{r})$  the IBO Coulomb-dipole functions. Here,  $\Omega$  are the Euler angles that specify the spatial orientation of the core,  $D$  is the matrix of the finite rotations, which coincides with the eigenfunction of the operator  $H^+$ , the asterisk denotes complex conjugation,  $\omega$  is the eigenvalue of the operator  $j_z$ ,  $\mathbf{r}$ ,

as before, are the Rydberg electron coordinates,  $k$  is the set of numbers  $\{\bar{s}, j, \omega, M_{\bar{s}}\}$ , where  $\bar{s}$  is the total momentum of the molecule minus the spin of the Rydberg electron ( $\bar{\mathbf{s}} = \mathbf{J} - \mathbf{s}$ ), and  $M_{\bar{s}}$  is the projection of  $\bar{\mathbf{s}}$  on the  $z$  axis. Then, the angular part of the Schrödinger equation can be recast as

$$2d\omega \sqrt{\frac{(2j+1)(2l'+1)}{j(j+1)}} \sum_{l''=l' \pm 1} C_{l'0 l''}^{l''0} W(j1\bar{s}l''; j l') a_{l''}^{(lk)} = [l'(l'+1) - \Lambda^{(lk)}] a_{l'}^{(lk)}. \quad (22)$$

Here,  $W$  is the Racah tensor, and  $\Lambda^{(lk)}$  is the eigenvalue of the system (22). Note that, in the IBO approximation, this system is finite, unlike the BO where the corresponding system (7) is infinite. The set of coefficients  $a_{l'}^{(lk)}$  is the eigenvector, which can be found by numerical solving Eq. (22). If  $d = 0$ , then  $\Lambda^{(lk)} = l(l+1)$ ,  $a_{l'}^{(lk)} = \delta_{ll'}$ , where  $\delta_{ll'}$  is the Kronecker  $\delta$ . It means that, for  $d = 0$ , the functions  $Z_{lk}^{\text{IBO}}$  are given by the familiar rules of the angular momentum algebra for two noninteracting subsystems. For  $d \neq 0$ , the values  $\tilde{l}$  and  $\mu_d$  can be introduced again as in Eqs. (8)–(10) with  $\lambda$  substituted by  $\Lambda$ . The graphs for several functions  $Z_{lk}^{\text{IBO}}$  are presented in Figs. 1–6. One can see that the influence of the core-dipole moment leads to the shift in the electron-density distribution due to attraction toward its positive-charge end repulsion from the negative-charge one. The results for the SO molecule are presented in Tables IV, V, and VII and are discussed in Sec. III. The radial function of the Rydberg electron  $R$  is given by the same formula (12).

 TABLE V. Quantum defect  $\mu_Q$  for the IBO region, Eq. (24).

| $j$ | $\bar{s}$ | $l$       |           |           |             |             |
|-----|-----------|-----------|-----------|-----------|-------------|-------------|
|     |           | 1         | 2         | 3         | 4           | 5           |
| 1/2 | 1/2       | 0         |           |           |             |             |
|     | 3/2       | 0         | 0         |           |             |             |
|     | 5/2       |           | 0         | 0         |             |             |
| 3/2 | 1/2       | -0.009 72 | -0.001 17 |           |             |             |
|     | 3/2       | 0.007 78  | 0         | -0.000 24 |             |             |
|     | 5/2       | -0.001 94 | 0.000 83  | 0.000 06  | -0.000 08   |             |
| 5/2 | 1/2       |           | -0.001 21 | -0.000 31 |             |             |
|     | 3/2       | -0.007 08 | -0.000 43 | -0.000 17 | -0.0001     |             |
|     | 5/2       | 0.0081    | 0.000 43  | 0.000 01  | -0.000 0402 | -0.000 0418 |

TABLE VI. Coefficients  $a_l^{(lm)}$  in the BO approximation for  $m = 0$ .

| $l$ | $l'$     |           |           |           |           |           |
|-----|----------|-----------|-----------|-----------|-----------|-----------|
|     | 0        | 1         | 2         | 3         | 4         | 5         |
| 0   | 0.885 67 | -0.457 45 | 0.079 25  | -0.007 02 | 0.000 38  | -0.000 01 |
| 1   | 0.460 73 | 0.844 60  | -0.270 91 | 0.031 48  | -0.001 98 | 0.000 08  |
| 2   | 0.057 58 | 0.277 41  | 0.941 60  | -0.181 39 | 0.014 54  | -0.000 67 |

Similar to Eqs. (14) and (15), asymptotical expressions for the dipole and quadrupole contributions into the quantum defect can be derived

$$\mu_d = -\frac{2(2j+1)}{j(j+1)(2l+1)}[W^2(j1\bar{s}l-1; jl) - W^2(j1\bar{s}l+1; jl)](d\omega)^2, \quad (23)$$

$$\mu_Q = \frac{\sqrt{(2j+1)(2l+1)}}{l(l+1)(2l+1)^2} C_{j\omega 20}^{j\omega} C_{l0 20}^{l0} W(j2\bar{s}l; jl) Q. \quad (24)$$

### C. Region of zero-dipole quantum defects

In the highest Rydberg states, the outer electron has only a small effect on the core stationary states, which are the components of the core  $\omega$  doublet, i.e., the symmetric and antisymmetric combinations of the core wave functions with different signs of  $\omega$ . In these stationary states, the average core-dipole moment is zero so that the Rydberg electron moves in a purely Coulomb field (provided, of course, that we have ignored the higher multipole moments and the short-range part of the core potential). Such a situation takes place if the following inequality is satisfied [40]:

$$n > n_\delta = (2\delta)^{-1/3}, \quad (25)$$

where  $\delta$  is the core  $\omega$ -doublet splitting. Thus, for  $n > n_\delta$ , the contribution of the core-dipole moment into the quantum defects of Rydberg states essentially is zero [40].

### III. NUMERICAL RESULTS FOR SO

Here, we present quantum defects and wave functions calculated using expressions (7), (15), (22), and (24) for the SO molecule. The constants of  $\text{SO}^+$ , necessary for the calculation, are the following: the dipole moment is  $d = 1.1$  a.u. [59], the rotational constant is  $B = 0.76$   $\text{cm}^{-1}$  [60], and the projection of the total momentum on the symmetry axis is  $\omega = 1/2$  [60]. The values of the quadrupole moment calculated with GAUSSIAN 09 using several methods and basis sets are presented

TABLE VII. Coefficients  $a_l^{(lk)}$  in the IBO approximation for  $j = \bar{s} = 5/2$ .

| $l$ | $l'$      |           |          |          |                       |
|-----|-----------|-----------|----------|----------|-----------------------|
|     | 0         | 1         | 2        | 3        | 4                     |
| 0   | 0.994 38  | 0.105 83  | 0.003 23 | 0.000 04 | $3.14 \times 10^{-7}$ |
| 1   | -0.105 87 | 0.993 33  | 0.045 79 | 0.00076  | $5.98 \times 10^{-6}$ |
| 2   | 0.001 64  | -0.045 88 | 0.998 56 | 0.027 59 | 0.000 28              |

in Table I, which gives the estimation  $Q \approx 0.75$  a.u. [61]. The results of the calculations for several Rydberg series in the BO and IBO approximations are shown in Tables II–VII.

Inequalities (1) and (17) give the border between BO and IBO regions,

$$n \sim (\mu/4Bj)^{1/3}. \quad (26)$$

Assuming  $\mu \sim 0.1$ – $0.01$  and  $j \sim 1/2$ – $19/2$ , one gets  $n \sim 4$ – $23$ . For  $n < 4$ , the BO approximation takes place, and the quantum defects for nonpenetrating Rydberg states are given by Eq. (10). The results are presented in Tables II and III. In Table II, the values of the dipole quantum defects are given. In Table III, the quadrupole quantum defects are presented, calculated following Eq. (15). In Table VI, the coefficients  $a_l^{(lm)}$  are presented. For  $n > 23$ , the IBO approximation takes place, corresponding quantum defects are given by Eqs. (22)–(24) and are presented in Tables IV and V, and coefficients  $a_l^{(lk)}$  and the change in the wave function are presented in Table VII and Figs. 1–6, respectively.

Next, we evaluate the width of the core  $\omega$  doublet with the use of the well-known formula for the  $X^2\Pi_{1/2}$  state [62],

$$\delta \approx \frac{AB}{\varepsilon}(j+1/2). \quad (27)$$

Here,  $A = 365$   $\text{cm}^{-1}$  is the spin-orbit coupling constant for the core ground state [63],  $\varepsilon \approx 25000$   $\text{cm}^{-1}$  is the distance to the first excited electron term of the core [64]. For  $j = 1/2$ – $19/2$ , it gives  $\delta \sim 0.01$ – $0.1$   $\text{cm}^{-1}$ . According to Eq. (25), the corresponding values are  $n_\delta \sim 100$ – $170$ . Thus, for  $n > 100$ – $170$ , the dipole part of the quantum defect is zero.

### IV. CONCLUSION

The energy regions of the BO and IBO approximations (discussed in Sec. II) represent spectral equivalents for familiar spatial regions  $A$  (near region) and  $B$  (far one) introduced by Fano in the molecular MQDT technique [15]. Indeed, the BO or IBO approximations take place when the Rydberg electron is localized in the region  $A$  or  $B$ , respectively. Hence, the BO Coulomb-dipole functions (4) and the IBO Coulomb-dipole functions (20) correspond to Fano's eigenfunctions  $X$  and  $\Phi$ , respectively (Eqs. (1)–(3) in Ref. [15]). The specifics of the present paper are that we explicitly take the effect of the core-dipole moment on the IBO wave functions (Fano's far-zone eigenfunctions  $\Phi$ ) into account. As can be understood from Eqs. (22) and (23), such an account is necessary when  $\omega \neq 0$ . This situation takes place for the SO molecule with the core ground state  $X^2\Pi_{1/2}$  considered in the present paper as well

as for a number of other molecules, such as NP, SiS, SiTe, etc. The proposed approach allows one to correctly include the effect of the core-dipole moment on quantum defects and the wave function of nonpenetrating Rydberg states of these molecules.

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