

# Potential energy curves of low-lying states of the CN molecule taking into account relativistic and quantum-electrodynamic corrections

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By the method of multireference configuration-interaction in the basis of Dirac-Fock-Sturm orbitals, a relativistic first-principles calculation of the potential energy curves of low-lying  $X^2\Sigma_{1/2}^+$  and  $A^2\Pi_{1/2}$  states of the CN molecule in the range of internuclear distances 0.8–8.0 Å has been performed. Using the method of the model Lamb shift operator, quantum-electrodynamic corrections to the total energy of the molecule for the given states have also been calculated. The contribution of quantum-electrodynamic corrections to the equilibrium internuclear distance  $R_{AB}^e$ , dissociation energy  $D_e$ , and vibrational constant  $\omega_e$  of the ground state of the CN molecule is considered.

**Keywords:** relativistic effects, correlation effects, quantum electrodynamic corrections, radical CN.

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## 1. Introduction

Among the most important diatomic molecules for astrophysics, the CN radical plays a special role, whose spectrum has been recorded in a wide variety of astronomical objects. For example, the spectra of carbon-rich stars contain lines corresponding to electronic transitions in the CN molecule [1]. Also, spectral lines of the CN radical have been detected in sunspots [2] and comets [3,4]. The CN absorption lines recorded in nuclei of galaxies may indicate active star formation [5]. The study of CN energy levels in molecular clouds in the interstellar medium allows us to study cosmic background radiation [6] and the isotopic composition and formation history of galaxies [7,8]. In addition, astrophysical spectroscopic data on the CN molecule can be used to study the variation of fundamental constants with time [9].

The structure of energy levels of the CN molecule has been examined numerous times both experimentally and theoretically. The most complete spectroscopic data are available for transitions between the three lowest CN doublet states: the so-called „violet“  $B^2\Sigma^+ - X^2\Sigma^+$  [10] and „red“  $A^2\Pi - X^2\Sigma^+$  [11] systems [12]. The theoretical study of spectroscopic properties of a molecule requires the construction of potential energy curves, which can be used to calculate vibrational contributions to the total energies of molecules. Semi-empirical methods, which utilize available experimental spectroscopic data, have been used widely to construct potential energy curves of different electronic states of the CN molecule [13–15]. Calculations of potential energy curves from first principles were also performed [16–19].

To further improve the accuracy of quantum-chemical calculations, it may be necessary to perform more accurate calculations of relativistic contributions and introduce quantum-electrodynamic (QED) corrections to the total energy of the molecule. For more exact calculation of relativistic contributions, it is necessary to go beyond the scalar-relativistic Douglas–Kroll approximation [20] and take into account spin-orbit splitting, which can be done, for example, with the use of the two-component Breit–Pauli Hamiltonian or the four-component Dirac–Coulomb–Breit Hamiltonian. As for the calculation of QED corrections, it should be noted that rigorous calculations of molecular QED corrections from first principles are a very difficult task and are currently only possible for one-electron and two-electron molecular ions [21–23]. However, QED effects can be accounted for with a sufficiently high degree of accuracy by the model-QED-operator [24–27] or the effective radiation potential [28–31]. In our recent work [32], the model operator method [24] was generalized to the calculation of the multi-electron QED corrections in the CO molecule.

Earlier in calculations of various properties of atoms and ions we widely used the relativistic method of multireference configuration-interaction in the basis of Dirac-Fock-Sturm orbitals (MRCI-DFS) [33–35]. In Ref. [32], this method was generalized to the case of calculations of the potential energy of diatomic molecules with closed shells. This work aims to extend the application of the MRCI-DFS method to molecules with open electron shells.

In the present work, potential energy curves for low-lying states  $X^2\Sigma_{1/2}^+$  and  $A^2\Pi_{1/2}$  of the CN molecule in the region of internuclear distances of 0.8–8.0 Å are obtained. QED corrections to the total energy of the  $X^2\Sigma_{1/2}^+$  and  $A^2\Pi_{1/2}$

states of the CN molecule are determined by the model-QED-operator approach [32]. In addition, the contribution of QED corrections to equilibrium internuclear distance  $R_{AB}^e$ , dissociation energy  $D_e$ , and vibrational constant  $\omega_e$  is obtained for the  $X^2\Sigma_{1/2}^+$  state of CN.

Atomic system of units is used herein ( $e = m = \hbar = 1$ ).

## 2. Theoretical methods

The MRCI-DFS method for calculations of diatomic molecules was discussed in detail in Ref. [32]. Here, we will describe the main points of this method. Adiabatic potential energy curves of the CN molecule were obtained in the present study using the Dirac–Coulomb (DC) Hamiltonian:

$$\hat{H}_{DC} = \Lambda^{(+)} [\hat{H}_D + \hat{V}_C] \Lambda^{(+)} \quad (1)$$

Here,  $\Lambda^{(+)}$  is the product of one-electron projectors to the positive spectrum of the Dirac–Fock (DF) operator,  $\hat{H}_D$  is the sum of one-electron Dirac Hamiltonians that contain the two-center potential created by nuclei

$$V_{AB}(\mathbf{r}) = V_{\text{nucl}}^A(\mathbf{r} - \mathbf{R}_A) + V_{\text{nucl}}^B(\mathbf{r} - \mathbf{R}_B), \quad (2)$$

and  $\hat{V}_C$  is the sum of two-electron operators of the Coulomb interelectron interaction. In potential (2),  $\mathbf{R}_A$ ,  $\mathbf{R}_B$  are the radius vectors of nuclei  $A$  and  $B$ , respectively. The model of a uniformly charged sphere nucleus was used to construct nuclei potentials  $V_{\text{nucl}}^{A,B}(\mathbf{r})$ . The values of mean-square radii of the nuclei were taken from Ref. [36].

At each given internuclear distance, many-electron wave function  $\Psi_\Omega$  of a molecule with a certain value of projection  $\Omega$  of the total angular momentum onto the internuclear axis is represented as a linear combination of Slater determinants

$$\Psi_\Omega = \sum_{\beta} C_{\beta}(\Omega) \text{det}_{\beta}(\Omega). \quad (3)$$

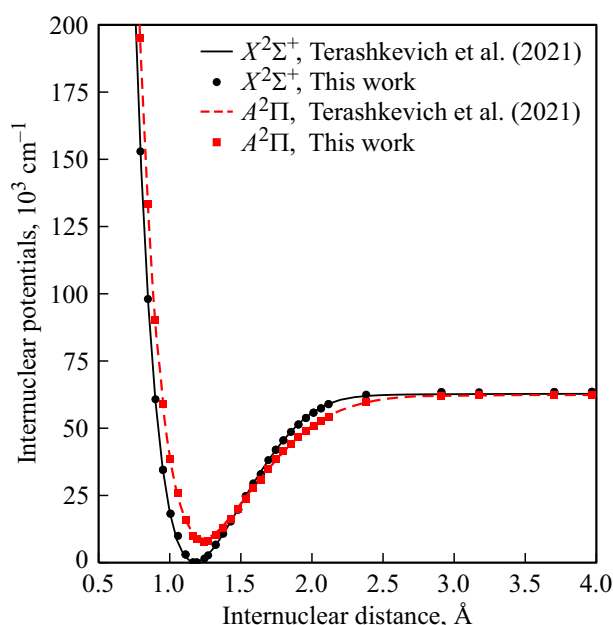
The problem of determining the coefficients of  $C_{\beta}(\Omega)$  reduces to the eigenvalue problem

$$H_{DC} \mathbf{C}(\Omega) = E_{DC}(\Omega) \mathbf{C}(\Omega), \quad (4)$$

where  $H_{DC}$  is the matrix of the DC Hamiltonian in the Slater determinants basis and  $\mathbf{C}(\Omega)$  is a column vector consisting of the coefficients of expansion (3).

The Slater determinants are constructed from one-electron molecular orbitals expanded in a two-center basis of DFS orbitals centered on different nuclei. The expansion coefficients of molecular orbitals in the DFS basis are determined by solving the two-center equations of the restricted DF method in matrix form (with orbitals with different-sign projections of the total angular momentum on the internuclear axis being populated equally).

When constructing the basis of one-electron DFS functions, orbitals of the basic configurations of carbon and nitrogen atoms were obtained first by solving the DF [37] equations numerically in the approximation of the center of



**Figure 1.** Dependence of the potential energy of the  $X^2\Sigma_{1/2}^+$  and  $A^2\Pi_{1/2}$  states of the CN molecule on the internuclear distance, which was calculated by the MRCI-DFS method, in comparison with the results of [18].

gravity of the nonrelativistic configuration [38]. At the next stage, we determined the virtual Sturm orbitals by solving numerically the Dirac–Fock–Sturm [33–35,39] equations.

QED corrections to the potential curves of the CN molecule were calculated using the model-QED-operator approach [24,25,40–42]. In calculations of QED corrections, the model operator was added to the Hamiltonian in the step of constructing the DFS basis, in solving the DF molecular equations, and in calculating the  $H_{DC}$  matrix. In other words, the model operator has been accounted for in all orders of perturbation theory. The QED energy correction was defined as the difference between the total electronic energies of the molecule with and without the model operator.

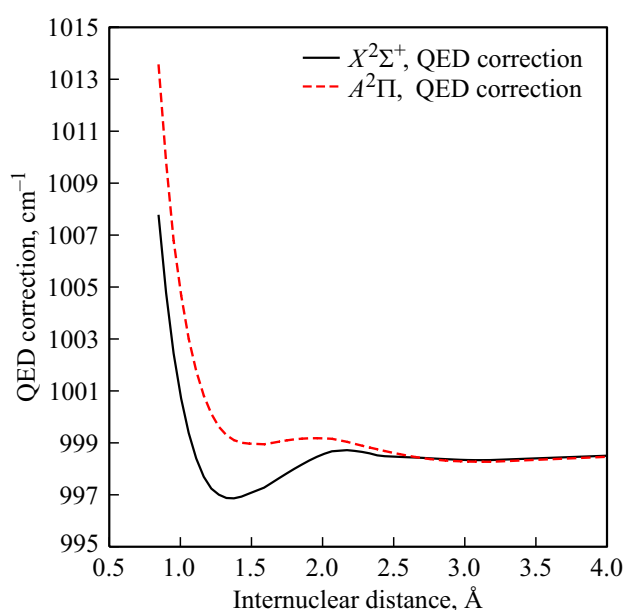
## 3. Calculation results

In the present work, adiabatic potential energy curves for two low-lying doublet states  $X^2\Sigma_{1/2}^+$  and  $A^2\Pi_{1/2}$  of the CN molecule were calculated using the MRCI-DFS method for inter-nuclear distances  $R_{AB} \in [0.8, 8.0]$  Å. All possible single and double excitations from all reference configurations to the space of active and virtual orbitals were taken into account in the construction of the MRCI matrix. Localized  $1s$  atomic orbitals were assigned to the frozen core. DFS atomic orbitals with principal quantum number  $n \leq 5$  and orbital quantum number  $l \leq 3$  of both atoms and, additionally, the  $6s$  orbital at each center were included into the one-electron basis.

Fig. 1 shows the results of calculation of the potential energy curves in the present study (black dots and red squares for states  $X^2\Sigma_{1/2}^+$  and  $A^2\Pi_{1/2}$ , respectively) and the curves obtained in Ref. [18] (black solid line and red dashed line for states  $X^2\Sigma_{1/2}^+$  and  $A^2\Pi_{1/2}$ , respectively). In Ref. [18], the curves of several low-lying CN states were calculated using the MOLPRO program. The potential energy curves in Fig. 1, as well as the QED plot in Fig. 2, are presented in the interatomic distance range up to 4.0 Å in order to render the region of minimum of the curves in more detail.

Comparison of the results of the present calculations with those of Ref. [18] shows good agreement for both states. The plot shows correct positions of the points both at small distances and in the region of the potential minimum and the dissociation limit. In addition, the intersection point of two potential curves at  $R_{AB} \approx 1.5$  Å is also consistent with Ref. [18]. Strictly speaking, in the relativistic calculation, two adiabatic curves shown in the plot cannot intersect, since they have the same projection of the total momentum on the molecule axis. However, in the nonrelativistic and scalar-relativistic approximations [18], they are molecular terms of different symmetry. Therefore, we have plotted our curves as intersecting nonrelativistic terms of different symmetry for clarity.

In the present study, QED corrections to the electronic energies of the CN molecule for the  $X^2\Sigma_{1/2}^+$  and  $A^2\Pi_{1/2}$  states were calculated by the model-QED-operator approach. The atomic orbitals of both centers with  $n \leq 4$  and  $l \leq 2$  were used as a one-electron basis in these calculations. Fig. 2 shows the results of calculation of QED corrections to the energies of states  $X^2\Sigma_{1/2}^+$  (black solid curve) and  $A^2\Pi_{1/2}$  (red dashed curve) of the CN molecule. The plot



**Figure 2.** Dependence of the QED corrections to the potential energy of the  $X^2\Sigma_{1/2}^+$  and  $A^2\Pi_{1/2}$  states of the CN molecule on the internuclear distance.

Equilibrium internuclear distance  $R_{AB}^e$  (Å), dissociation energy  $D_e$  ( $\text{cm}^{-1}$ ), and vibrational constant  $\omega_e$  ( $\text{cm}^{-1}$ ) for the ground state of the CN molecule obtained in this work without QED corrections (2nd column) and with QED corrections (3rd column). The fourth and fifth columns present the data from Ref. [11] and Ref. [17], respectively

| Value                      | DC      | DC + QED | [11]   | [17]    |
|----------------------------|---------|----------|--------|---------|
| $R_{AB}^e, \text{Å}$       | 1.177   | 1.177    | 1.172  | 1.171   |
| $D_e, \text{cm}^{-1}$      | 61640.1 | 61641.0  | -      | 63083.8 |
| $\omega_e, \text{cm}^{-1}$ | 2119.9  | 2120.1   | 2068.7 | 2069.3  |

shows that the depth of the minimum of the QED correction curve for the  $X^2\Sigma_{1/2}^+$  state relative to the long-range limit is very small: less than  $2 \text{ cm}^{-1}$ . However, as the interatomic distances decrease, the magnitude of QED contributions increases dramatically.

Finally, for the ground state of the CN molecule, we calculated the contributions of QED corrections to the values of certain molecular constants, namely equilibrium internuclear distance  $R_{AB}^e$ , dissociation energy  $D_e$ , and vibrational constant  $\omega_e$ . The values of  $R_{AB}^e$  and  $\omega_e$  were determined in OpenMolcas with the use of the adiabatic curves calculated in this work. Dissociation energy  $D_e$  was defined as the difference between the total energies of the molecule at  $R_{AB} = 8.0$  Å and at the point of minimum  $R_{AB}^e$ . The values of  $R_{AB}^e$ ,  $D_e$ , and  $\omega_e$  were determined both without and with QED corrections.

The results of calculation of equilibrium internuclear distance  $R_{AB}^e$ , dissociation energy  $D_e$ , and vibrational constant  $\omega_e$  for ground state  $X^2\Sigma_{1/2}^+$  of the CN molecule are presented in the table without (2nd column) and with (3rd column) QED corrections. The data from Ref. [11] and Ref. [17] are also listed in the table for comparison with our calculations. In Ref. [11], spectroscopic constants of the CN molecule were derived from the analysis of experimental data; in Ref. [17], they were determined with the use of adiabatic curves calculated by the MRCI method in MOLPRO.

The table shows that QED corrections provide a very small contribution to the value of the internuclear distance. The value of  $R_{AB}^e$  is 1.777 Å both with and without QED corrections. Notably, our  $R_{AB}^e$  value matches well the equilibrium distances of 1.172 Å from Ref. [11] and 1.171 Å from Ref. [17]. The value of dissociation energy  $D_e$  without QED corrections is  $61640.1 \text{ cm}^{-1}$ , which differs from the result of [11,17] by about 2%. The contribution of QED corrections to the value of  $D_e$  is approximately  $1 \text{ cm}^{-1}$ . The value of vibrational constant  $\omega_e$  obtained in this work without QED corrections is  $2119.9 \text{ cm}^{-1}$ , while QED corrections contribute about  $0.2 \text{ cm}^{-1}$ . Our result differs from the data of Refs. [11,17] by about 2%.

## 4. Conclusion

In this paper, a relativistic non-empirical calculation of potential energy curves for states  $X^2\Sigma_{1/2}^+$  and  $A^2\Pi_{1/2}$  of the CN molecule in the region of internuclear distances  $R_{AB} \in [0.8, 8.0] \text{ \AA}$  was carried out by the method of multireference configuration interaction in the basis of Dirac–Fock–Sturm orbitals. The obtained data agree well with the results of earlier studies. In addition, QED corrections to the total energy of the  $X^2\Sigma_{1/2}^+$  and  $A^2\Pi_{1/2}$  states of the CN molecule were calculated using the model-QED-operator approach. The obtained dependence of QED corrections on the internuclear distance was used to determine the contribution of QED corrections to equilibrium internuclear distance  $R_{AB}^c$ , dissociation energy  $D_e$ , and vibrational constant  $\omega_e$ .

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## Conflict of interest

The authors declare that they have no conflict of interest.

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