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Relativistic, quantum-electrodynamic and electron-correlation corrections to the interatomic potential of the CN radical

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The dependence of the ground-state ($X^2\Sigma^+$) potential energy of the CN molecule on the internuclear distance was determined using the single-reference coupled-cluster method. Contributions to the electronic energy arising from relativistic effects, including spin-orbit interaction and the Gaunt correction, as well as quantum electrodynamics corrections implemented through a generalized relativistic pseudopotential model, were evaluated. The incorporation of these factors resulted in good agreement between the calculated equilibrium bond distance R_e and harmonic vibrational frequency ω_e with experimental data.

Keywords: relativistic effects, electron-correlation corrections to the interatomic potential of the CN radical.

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Introduction

A chemically active (due to the presence of an unpaired electron) diatomic CN molecule forms easily at high temperature in various aeronomic, space and laboratory media by collisional and radiative association of carbon and nitrogen atoms in both the bound and free states. Besides, a CN radical is formed as a result of the photodissociation of most cyanide-containing compounds, such as isomers of HCN/NCH molecule, which are common in many regions of space. A cyanoradical (CN) is one of the first molecules found in the interstellar medium [1], and plays a key role in studying the physical and chemical processes in space.

Optic, infrared and microwave spectra with participation of the main electron state of CN isotopomers are observed in many space objects, such as interstellar clouds and comet comas, as well as in carbon stars, and, possibly, in exoplanet atmospheres [2–4]. Observations of CN astronomical spectra are important for monitoring star-formation processes and for an alternative determination of the temperature of the cosmic microwave background radiation (relic radiation) by measuring the intensities of several low-lying $\mathrm{X} \rightarrow \mathrm{B}$ electronic transition lines. Registration and analysis of CN astronomical spectra may also help to understand the processes of nucleosynthesis and the origin of the elements in the Universe [5–8].

In addition, CN molecules are often produced during the convective thermal ablation of spacecraft in hypersonic airflows as they enter planetary atmospheres, such as those of Earth and Titan, as well as in ground-based laboratory experiments using high-energy shock-tube facilities. CN radicals are also formed in significant quantities in air when laser-induced breakdown spectroscopy is used for elemental and isotopic analysis of carbon-containing organic and inorganic samples.

It is well-known that experimental spectra of CN are characterized by the observation of a large number of both regular and local intramolecular disturbances [10–12], which severely complicates their unambiguous interpretation at the currently required spectroscopic level of precision [13]. To model such „disturbed“ spectra, no usually here a reduced method of oscillating channels is usually used [14,15], which requires precise a priori knowledge of diagonal and non-diagonal matrix elements of the electron Hamiltonian of the molecule in the form of express functions of the internuclear distance [16]. It is evident that this requirement can only be achieved within non-empirical quantum-chemical calculations of very high level. Therefore, the most comprehensive account of various electron-correlation and relativistic effects in calculation of electron structural parameters of molecules (first of all, potential energy curves) in the wide range of its geometric parameters is a relevant problem in contemporary theoretical spectroscopy.

Due to its high practical value, the CN molecule has been studied in detail by *ab initio* quantum chemistry methods in many papers, the detailed list of which is presented, for instance, in [17]. Currently, the most widely used approach for calculating the CN molecule is a combination of the multi-configuration self-consistent field method in the complete active space (CASSCF) and internally contracted version of the multi-reference configuration interaction (ic-MRCI) method, augmented with the correction (ic-

MRCI+Q) [17–21], or the size-consistent modification of the configuration interaction method — multi-reference averaged coupled-pair functional method (MR-ACPF) [16]. Such calculations are usually performed using different two-component Hamiltonians, which do not take into account the spin-orbital interaction. In the literature, such an approach is called a scalar relativistic approximation. In the papers [17,19] the authors achieved very high precision in the determination of the spectroscopic constants, therefore it becomes necessary to consider the corrections beyond the used approximations.

Paper [22] studied the applicability of the single-reference coupled cluster (SR-CC) method to calculate the potential energy curve (PEC) of the CN molecule in the range of interatomic distances $R \leq 1.8\,\text{Å}$. The authors considered the effect of triple (CCSDT) and quadruple (CCSDTQ) excitations in addition to the standard consideration of single and double excitations (CCSD), as well as the full fonfiguration interaction (FCI) method to obtain the reference energy values. However, the accuracy of the calculations in [22] was limited by the use of small basis sets (cc-pVDZ and cc-pVTZ [23]), which prevented the achievement of the current precision standards.

In this paper, a number of key corrections affecting the PEC of the CN molecule ground state ($X^2\Sigma^+$) are investigated by the SR-CC method. The primary focus of this study is the account of non-perturbative triple excitations (T), relativistic effects, including spin-orbit interaction and Gaunt correction, and quantum-electrodynamic (QED) effects. These corrections play an important role in precise modeling of CN molecule's energy profile.

To account for relativistic effects, the four-component Dirac–Coulomb Hamiltonian was used. The QED correction value is obtained using the model QED operator and generalised relativistic pseudopotential (GRPP) methods [24,25], and a comparison with the results presented in a recent paper [26] has been made..

Calculation details

To calculate potential energy curves, the single-reference coupled cluster method was used with the Dirac–Coulomb (DC) Hamiltonian. This combination provided an accurate account of relativistic effects. The calculations were performed using the DIRAC software package [27,28] and aug-cc-pVnZ series basis sets ($n = 3, 4, 5$) [23,29].

To improve the precision, the results were extrapolated to the complete basis set limit (CBS) [30]. A three-point formula with $n = 3, 4, 5$ was used for the energy at the Dirac–Fock (DF) level:

$$E_{\text{DHF}}(n) = E_{\text{DHF}}^{\text{CBS}} + Ae^{-\beta n}, \tag{1}$$

two-point formula $n = 4, 5$ was used for correlation corrections:

$$E_{\text{corr}}(n) = E_{\text{corr}}^{\text{CBS}} + \frac{A}{n^3}. \tag{2}$$

All 13 electrons of the CN molecule were correlated in the calculations. Virtual orbitals with energy up to 300 a.u. were considered, which corresponds to 266 virtual orbitals and provides sufficient accuracy for calculations within the considered approach. The range of internuclear distances was limited to the interval from 0.6 to 1.87 Å due to poor convergence of the method at larger/smaller internuclear distances.

The CN molecule is an open-shell system, for which the ground state configuration near the equilibrium position, $X^2\Sigma^+$, may be written as $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^1$. Due to the change in the order of the molecular orbitals at large internuclear distances, the lowest energy configuration becomes $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^3$, which corresponds to state $A^2\Pi$. These states intersect at an internuclear distance of around 1.5 Å [16].

The solution with the correct configuration at the DF level is obtained by selecting a suitable initial approximation that depends on the internuclear distance. This provides for best initial approximation for SR-CC method. It is worth noting that during the computations, convergence issues at the DF level were observed at certain internuclear distances, as well as large amplitudes in the coupled cluster method, making it challenging to apply the SR-CC approach.

The consideration of triple excitations by perturbation theory for open-shell systems can lead to incorrect results. Therefore, the contribution of non-perturbative triple excitations $\Delta E^{\text{T}} = E_{\text{CCSDT}} - E_{\text{CCSD}}$ has been calculated in this work. The calculations were performed in the EXP-T program [31,32] using the aug-cc-pVTZ basis set with nine electrons correlated and 92 virtual orbitals included.

The relativistic correction was calculated as the difference between the energies obtained in two SR-CC calculations, using Dirac–Coulomb and non-relativistic Hamiltonians. The calculations were performed with the aug-cc-pVQZ basis set. The correlations of all 13 electrons of the system were taken into account, and the number of virtual orbitals was set to 166, which corresponds to energy threshold of 50 a.u.

The coupled cluster method in Fock Space (FS-CC) with X2C Hamiltonian was employed to calculate the Gaunt correction [33,34]. The ground state of the CN^- ion was designated as the sector (0,0), which ensures optimal convergence at large internuclear distances. The ground state energy of the CN molecule was determined by solving the FS-CC equations in the (1,0) sector using the aug-cc-pVQZ basis set. In the calculation, all 14 electrons were correlated, and the number of virtual orbitals was set to 161.

To estimate QED effects, PECs of the CN molecule were calculated using generalized relativistic pseudopotentials (GRPP) [24,25]. The use of GRPP allows one, in particular, to effectively account for interaction with core electrons, relativistic corrections, the Breight interaction, etc. The QED correction was obtained by calculating the difference between two sets of calculations: one set utilized GRPPs constructed with QED effects, and the other set utilized

Table 1. Basis set convergence of the equilibrium internuclear distance, R_e, and the harmonic vibrational frequency, ω_e, of the CN molecule

n	R_e, Å	ω_e, cm^{-1}
3	1.1360	2714
4	1.1648	2235
5	1.1632	2238
CBS	1.1615	2139

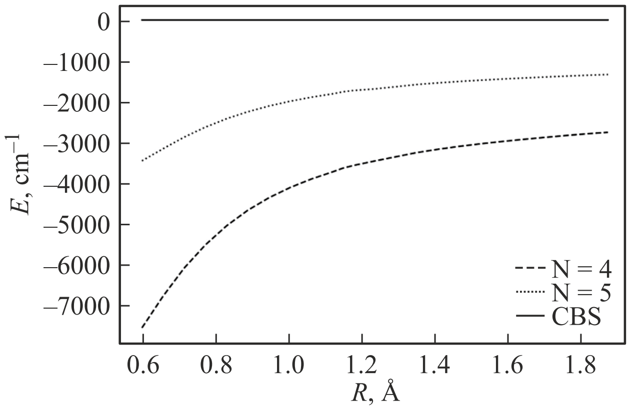

Figure 1. Convergence of the ground-state energy of the CN molecule with respect to basis set. The results are presented for the aug-cc-pVnZ basis set family with respect to the CBS values in the CCSD approximation.

GRPPs constructed without QED effects. The GRPP, which incorporates QED effects, is formulated within the framework of the model-QED-operator approach. This approach encompasses vacuum polarisation and self-energy operators [35,36]. The calculations were performed using the DIRAC software [27,28] and the LIBGRPP library [25], which is necessary to account for the non-local part of the potential. We have succefully applied this approach to the calculation of QED corrections in the CO molecule [37,38].

Results and discussion

Fig. 1 shows the convergence of the ground-state energy calculated by the CCSD method using various basis sets of the aug-cc-pVnZ series ($n = 4, 5$). The energy is counted from the extrapolation result to the limit of the complete basis set.

The dependence of the equilibrium distance R_e and the harmonic vibrational frequency ω_e of the CN molecule on the basis set is presented in table 1. All data were obtained on the basis of PEC analysis performed in the OpenMolcas software [39].

Fig. 2 presents the calculated PECs of the CN molecule obtained at different levels of electron correlation treatment: CCSD and CCSDT, as well as semi-empirical curve from paper [10]. For comparison purposes, all curves were aligned at the equilibrium internuclear distance.

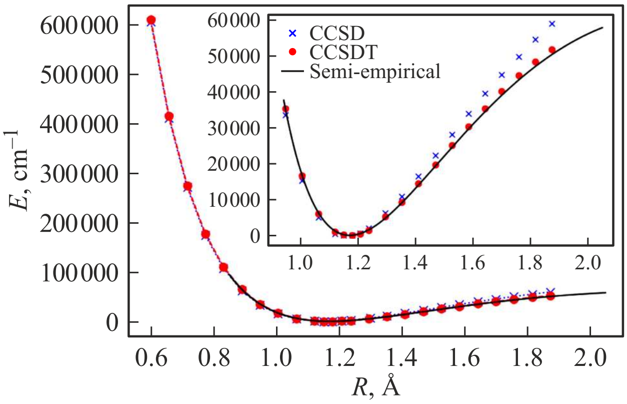

Figure 2. Potential energy curves of the CN molecule obtained at different levels of correlation effects accounting: CCSD and CCSDT, as well as semi-empirical curve from the paper [10].

The analysis shows that near the equilibrium internuclear distance, the differences between the methods are minimal, and all curves demonstrate good agreement. However, as the internuclear distance increases, a significant contribution from the triple excitations (T) becomes apparent, which significantly corrects the curve shape. Taking this contribution into account in the CCSDT method gives a better agreement with the semi-empirical curve and with the experimental spectroscopic data, confirming the importance of high order excitations for an accurate modeling of the PEC, which agrees with the results of paper [22].

Relativistic effects were analyzed by comparing calculations performed using the DC Hamiltonian and the non-relativistic Hamiltonian. The relativistic contribution, as well as its sum with the Gaunt correction to the PEC are shown in fig. 3. The contribution of the relativistic correction to the curve shape does not exceed $1000\,\mathrm{cm}^{-1}$, and of the Gaunt correction — $300\,\mathrm{cm}^{-1}$. The contribution is most significant at internuclear distances of less than 1 Å. The result of QED correction estimation obtained using GRPP is shown in fig. 4. The QED correction calculated in this paper demonstrates the specific minimum near the equilibrium distance of the CN molecule. The magnitude and the behavior of the correction differ from the results presented in paper [26]. Nevertheless, both curves show that the contribution of the QED correction provides negligible influence on the overall shape of the cyanoradical potential energy curve.

Based on the obtained PECs, the equilibrium distance R_e and the harmonic oscillation frequency ω_e (table 2) were calculated. As previously mentioned, incorporating triple excitations substantially improves the curve description, which is confirmed by the better agreement of values R_e and ω_e with the experimental data. The contribution of the Gaunt correction to the equilibrium internuclear

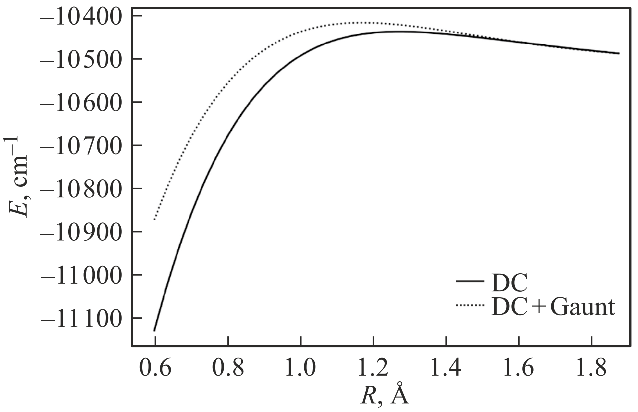

Figure 3. Relativistic corrections to the ground-state PEC of the CN molecule. The solid line corresponds to the contribution due to the DC Hamiltonian with respect to the nonrelativistic Hamiltonian, the dashed one — to the sum of DC contribution and Gaunt correction.

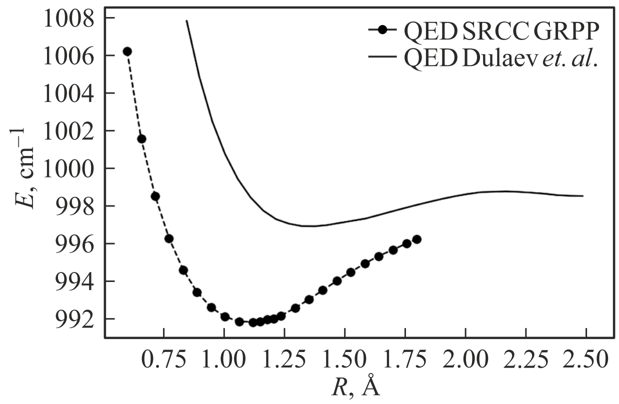

Figure 4. Quantum-electrodynamic corrections to the ground-state PEC of the CN molecule. The solid line corresponds to the data obtained in paper [26].

Table 2. The calculated values of the equilibrium distance R_e and the harmonic vibration frequency ω_e of the CN molecule by the CCSD method with the addition of the triple excitations contribution (T) and Gaunt correction (G). The values obtained by the ic-MRCI+Q method and the experimental data [3] are given for comparison.

Method	R_e, Å	ω_e, cm^{-1}
CCSD	1.1615	2139.00
CCSDT	1.1729	2070.16
CCSDT+G	1.1731	2069.77
ic-MRCI+Q[a]	1.1714	2069.26
MR-ACPF[b]	1.1746	2060.53
Experiment	1.1718	2068.59

Note. [a] Yin *et.al.* [17].

[b] The data were obtained by PEC approximation from paper [10] in the OpenMolcas software.

distance is around 0.0002 Å, and to the harmonic oscillations frequency — around 0.4 cm^{-1}.

The discrepancy between the R_e and ω_e values and the experimental data from paper [3] is around 0.001 Å and 1 cm^{-1}, respectively, which is somewhat inferior to the values obtained by the ic-MRCI+Q method in paper [17]. Achieving high accuracy in SR-CC requires accounting for higher-order excitations and using the basis sets that improve core-electron correlation, such as the aug-cc-pCV*n*Z series.

Conclusion

In this work, the PEC of the ground state of the CN ($X^2\Sigma^+$) molecule was calculated. The emphasis of the study was directed towards the consideration of corrections that affect the shape and accuracy of the PEC. In addition to the standard accounting of single and double excitations, nonperturbative triple excitations were included, which turned out to be especially significant at large internuclear distances. This highlights the necessity to consider higher-order excitations to achieve more precise modeling of the molecule's energy profile.

The relativistic effects, including spin-orbital interaction and Gaunt correct, were studied. The generalized relativistic pseudopotential method, incorporating the model-QED-operator, was employed to account for QED effects. The relativistic correction makes the most important contribution to PEC, especially at small internuclear distances. The contribution of the Gaunt correction to the spectroscopic constants lies within the error margin of current theoretical results and can therefore be used to refine them. The QED correction provides no significant effect on the shape of the PEC, and its contribution to the spectroscopic constants is negligible.

In general, our results demonstrate good agreement with the previous theoretical calculations and experimental data for such key parameters as equilibrium distance R_e and harmonic vibrational frequency ω_e, and the shape of the obtained PEC agrees well with the semi-empirical curve from paper [10].

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Conflict of interest

The authors declare that they have no conflict of interest.

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