Diffusion and reptation quantum Monte Carlo study of the NaK molecule

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Diffusion Monte Carlo (DMC) and Reptation Monte Carlo (RMC) methods, have been applied to study some properties of the NaK molecule. Hartree-Fock (HF), Density Functional (DFT) and single and double configuration interaction (SDCI) wavefunctions with a valence quadruple zeta atomic natural orbital (VQZ/ANO) basis set were used as trial wavefunctions. Values for the potential energy curve, dissociation energy and dipole moment were calculated for all methods and compared with experimental results and previous theoretical derivations. Quantum Monte Carlo (QMC) calculations were shown to be useful methods to recover correlation in NaK, essential to obtain a reasonable description of the molecule. The equilibrium distance yield a value close to the experimental one. The dissociation energy, however, is not so good, and the minimum error is about 4% of the experimental value, except when a coupled-clusters method is used. In this case, a conventional CCSD(T) calculation with an extended aug-pc-4 basis set gives a much better agreement to experiment. However, neither the CCSD(T) nor other MO and DFT methods are able to reproduce correctly the large dipole moment of this molecule. Even DMC methods with a simple HF trial wavefunction are able to give a better agreement to experiment, although they have a larger error bar.

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I. INTRODUCTION

One of the technologies that will shape our not so distant future—along virtual reality, artificial intelligence, androids and the like—will be quantum computing. Some years ago, Yelin et al. suggested schemes for robust quantum computation using polar molecules. More recently, Kuznetsova, in the same group, analyzed the experimental feasibility of polar molecule based phase gates, determining the requisites for a polar molecule qubit system. In their study they used the CO molecule, but other lines of research have pointed toward alkaline molecules.

New experimental techniques for the formation of polar molecules in their rovibrational ground states, namely stimulated rapid adiabatic passage (STIRAP) and Feshbach-optimized photo-association (FOPA), have allowed the study of ultracold (v=0) uncommon alkali diatomics, like LiCs, KCs or KRb. There has been increased interest in the last ten years on these ultracold (formed below 1 mK) molecules, since their unusually large dipole moment allow them to be controlled by electric fields, promising new applications in quantum computing, ultracold chemistry, new phases of matter and precision measurements. Several theoretical studies have also appeared on the structure and properties of these molecules, a difficult task because the bond is a relatively weak van der Waals interaction, with large equilibrium bond distances and dipole moments and small dissociation energies.

NaK is one of the heteronuclear alkali diatomic molecules that had been thoroughly investigated in past years. Ross published a study of the ground X1Σ+ state using Fourier-transform infrared spectroscopy, while Wormsbecher and Yamada performed high resolution microwave spectroscopy experiments, obtaining values of 3.4990348(15) Å for the equilibrium distance (confirmed later by LIF experiments) and 2.73 D for the dipole moment. The dipole moment of NaK had been previously determined experimentally as μ0(39K23Na)=2.76±0.1 D by Dagdigian and Wharton. It was later shown that the potential energy curve (PEC) derived by Ross from his experimental results was faulty. Russier-Antoine, Ross et al. reanalyzed the data and derived an improved PEC in 2000. The dissociation energy estimated in this work was 5273.78±0.24 cm⁻¹ (24.029±0.001 mhartrees). Gerdes et al. performed recently a simultaneous analysis of the lowest X1Σ+ and a3Σ⁺ electronic states of the NaK molecule, confirming the equilibrium distance Re=3.4990 Å and a dissociation energy of 5273.62±0.10 cm⁻¹ (24.0284±0.0004 mhartrees).

Some recent theoretical research has been performed also on this molecule. On the one side, Zemke et al. used the CCSD(T) method with the McLean-Chandler 6-311+G(3df) basis set to calculate the interaction of Na2, K2 and NaK dimers. Their calculations afforded values of 3.488 Å for the equilibrium distance and 2.94 D for the dipole moment of NaK. Another important paper on this subject was published by Byrd et al. They used also the CCSD(T) method, but with the explicitly correlated F12b theory—which allows for greater precision—for the study of K and Rb clusters. Byrd et al.
studied also the PECs of homonuclear alkali metal diatomics using single excited configuration interaction (CIS) and time dependent density functional methods (TD-DFT) using the B3PW91 and PBE0 potentials. Aymar and Dulieu used a 7s5p5d2f /5s5p3d2f contracted basis set for Na and a 7s5p7d2f /6s4p4d2f contracted basis set for K in order to perform CI calculations of the dipole moment, including a pseudopotential to represent the atomic cores and a phenomenological potential to describe core polarization. They found a dipole moment of 2.76 D at an optimum equilibrium distance of 3.440 Å. Finally, Fedorov et al. have recently determined accurate potential energy, dipole moment curves, and lifetimes of vibrational states of heteronuclear alkali dimers, including NaK. They used all-electron quadruple-ζ basis sets with additional core functions for sodium, and small-core relativistic effective core potentials (ECP) with quadruple-ζ quality basis sets for potassium. An important conclusion of their work is that non-perturbative triples (i.e. CCSDT) are necessary for obtaining quantitative agreement between calculated and experimental results.

In this work we aimed to describe the bond length, dipole moment and dissociation energy of the NaK molecule from two complementary points of view. On one side, we performed DFT calculations (PBE0) with and without an empirical dispersion correction, as well as CCSD(T) calculations to study the PECs of NaK and some of its properties at equilibrium, in order to stablish the link between former theoretical calculations and our own. On the other side, we used three versions of the quantum Monte Carlo (QMC) method, namely Diffusion Monte Carlo (DMC), Reptation Monte Carlo (RMC) and Variational Monte Carlo (VMC) to study the NaK molecule ground state. The QMC calculations used trial wavefunctions calculated at the monoconfigurational (Hartree-Fock) and multiconfigurational (MCSCF and CISD) levels, as well as several DFT methods (B3LYP, PBE and BHHLYP). PECs, equilibrium distances, dipole moments and dissociation energies were calculated and compared both with experimental values and results from other theoretical calculations. The results show that the VMC calculations combined with DMC give a result for the dissociation energy (23.0 and 25.2 mhartrees at the CISD and CASSCF based QMC levels) not very far from the experimental result (about 4%). RMC is necessary however to improve the agreement of the calculated dipole moment with the experimental value. Systematic improvements in QMC are observed both when using multideterminant wavefunctions or fixed node approximations (FNA) corrections such as backflow. Possible deficiencies due to the use of pseudopotentials and small basis sets are discussed.

II. COMPUTATIONAL METHODS

A. Conventional calculations

Molecular orbital and DFT methods were used for calculating the potential energy curves (PEC) and to compare them with previous studies. Hartree-Fock (HF), coupled clusters single, double and perturbative triples(CCSD(T)), complete active space self consistent field (CASSCF) and multi-reference configuration interaction procedures were employed, using
mainly the Kalsruhe Def2-QZVPPD basis set\textsuperscript{20}, both for Na and K. All electron (i.e. no pseudopotential) calculations were performed, but only valence electrons were correlated at the post-HF levels in the PEC calculations. All electrons were included however, in the CASSCF and MRCI calculation of the optimum equilibrium distance and properties at this geometry. DFT calculations of the PEC were performed using the PBE0 method\textsuperscript{21} with and without the GD3 empirical dispersion correction by Grimme\textsuperscript{22}. Dissociation energies were obtained from the curves with respect to the asymptotic limit, both to avoid the need of BSSE (basis set superposition energy) corrections and the spin-orbit corrections due to the radical nature of the Na and K atoms. Geometry optimizations were performed to obtain the equilibrium distance and the dipole moment of the corresponding structure. All conventional calculations were performed using the G09\textsuperscript{23} and Molpro\textsuperscript{24} set of computer programs. Basis set dependency of the calculations was tested for the PBE0 and CCSD(T) methods employing the Def2-QZVP and Def2-TZVP Kalsruhe basis sets, as well as Feller quintuple-zeta pc-4 basis set\textsuperscript{25, 26}.

B. Monte Carlo calculations

QMC calculations were performed on the NaK starting from the experimental bond length. The QMC method is able to give the exact ground state energy if the fixed-node approximation (FNA) is used (necessary to maintain the fermionic nature of the wave function).\textsuperscript{27, 28, 29, 30, 31, 32} Thus, fixed-node diffusion Monte-Carlo is the most common variant of QMC in use\textsuperscript{33, 34}. DMC calculations are started using a trial function, which can be a single Slater determinant or a multideterminantal wavefunction\textsuperscript{35}. This function can be obtained either from molecular orbitals or from DFT Kohn-Sham orbitals. If the nodal surface of the trial wave function were exact, then the DMC method, if run for a large enough number of steps and extrapolated to zero timestep, would give the exact ground state energy. This is obviously not the case when using a single determinant MO wavefunction, although for some systems it may be a good approximation. All the QMC simulations in this work were done using an energy-consistent scalar-relativistic Hartree Fock pseudopotential (BFD)\textsuperscript{36} with a VQZ/ANO basis set, using HF and a pair of DFT functionals (B3LYP, PBE) to build the trial wavefunction. The influence of a multideterminantal wavefunction was explored by CASSCF(10,10) calculations, on top of which a second order configuration interaction (SOCI)—including all single and double excitations—was performed.

As a brief summary of the QMC method used in this paper, we will follow the description given by Kim et al\textsuperscript{37}. Given an $N$-electron system in a state described by a $3N$-dimensional wave function $\Psi(r_1, ..., r_N)$ satisfying the usual time-independent Schrödinger equation, $\hat{H}\Psi = E_0\Psi$, with a hamiltonian including the kinetic and potential energy of interaction of the particles, QMC methods employ a trial function $\Psi_T$, which takes the general form

$$\Psi_T(R) = \sum c_i D_{iu} D_{id} e^{J}$$

(1)
where $J$ is the Jastrow factor, and the $D_i$ are Slater determinants with spin up (u) or down (d) of an N electron wavefunction.

The energy of the system can then be evaluated as

$$E_T = \int \frac{d^N R \bar{\psi}_T(R) \bar{\psi}(R)}{\int d^N R |\psi_T(R)|^2}$$  \hspace{1cm} (2)

This is a general equation, which in the case of QMC is estimated by stochastic sampling as

$$E_T \approx \frac{\sum_i w(R_i) E_L(R_i)}{\sum_i w(R_i)}$$  \hspace{1cm} (3)

where $E_L$ is a local energy, evaluated as

$$E_L = \bar{H}\psi_T(R)/\psi_T(R)$$  \hspace{1cm} (4)

and the $w$ are weights at point $R$. The $R_i$ are the configurations and they are distributed according to the mixed density, which in turn is calculated as a combination of the trial wavefunction and the exact one (estimated in DMC). In our case we took all weights equal to 1.

The trial wavefunctions, modified by the inclusion of a two-body Slater-Jastrow factor $^{38}$, were $\alpha$-optimized using the VMC method. DMC calculations were then performed, applying the Green’s function technique $^{27}$, using a 0.01 timestep and the T-moves Casula’s correction $^{39}$, aimed to go beyond the locality approximation in standard DMC and restoring the variational property in the computed energy. In the case of multideterminantal SOCI/CASSCF(10,10) wavefunctions, configurations were included with different cutoff limits for the weights (from 0.1 to 0.001). In this case, the CI coefficients and the Jastrow parameters were optimized together. The QMCPACK program $^{40}$ was used to perform both the VMC and DMC calculations.

DMC works by producing an ensemble of replicates of the system, called walkers. The process consists in moving the electrons of each walker in imaginary time through Langevin diffusion (the propagator approach). The resulting configuration is subject to physical branching (a death-birth process). In these conditions, a DMC iterative process, if left to run for an infinite time, would lead to infinite number of walkers or none at all. For that reason, an artificial procedure is included, called population control, where the physical branching is so designed as to yield a number of walkers that oscillates around a mean value $^{41}$, or alternatively by fixing the number of walkers $^{42}$, using weight-branching. In this work, population control was tested using 9600, 19200, 38400 and 76800 configurations.

An alternative method is called reptation quantum Monte-Carlo (RMC) $^{43}$. In this case, the Metropolis algorithm is used to decide the branching (a randomly produced configuration is accepted or rejected by the use of a threshold). RMC gives
pure estimates of properties which operators do not commute with the Hamiltonian. RMC is free from population control and it is known from the literature to afford better results for observables than DMC in certain cases.

When analyzing the RMC results one has to keep in mind the meaning of the parameters that affect the quality of the RMC projection. On one side we have the imaginary projection time $\beta$ for the sampling path (the size of the reptile) on the other the Trotter time step $\tau$. $\beta$ needs to be large enough so that the projections of the trial function $\Psi_T$ give a good approximation to the true wavefunction, both for mixed and pure observables. The approximate equations to be fulfilled is

$$e^{-\beta \hat{H}} |\Psi_T\rangle \approx |\Phi_0\rangle$$

The reptile is discretized into the number of bits $N=\beta/\tau$ called “beads” (an odd number is selected so that there is a central bead). This process gives an error in the observables that is directly proportional to $\tau$, reason for which this parameter should be reasonably small. At the same time, the larger the $\beta$ is, the more difficult is the calculation since larger reptiles have to be propagated.

In this work we used the RMC method with a 45 hartree$^{-1}$ reptile length, with the specific aim to get a better estimation of the dipole moment. Both RMC and DMC calculations of the dipole moment were performed with $\tau$=0.01 hartree$^{-1}$, which was converged within error bars, and for our RMC calculations, we chose $N$=4501 (which corresponds to the 45 hartree$^{-1}$ long projection length). These calculations were performed using the QWalk code. Due to some limitations of this program, the QZ basis set used in the DMC calculations could not be employed and a TZ basis set was used instead.

**III. RESULTS AND DISCUSSION**

**A. Results obtained using MO and DFT methods.**

PECs obtained at the HF, CCSD(T), CASSCF(10,10) and MRCI/CASSCF(10,10) levels, with the Karlsruhe basis sets, are shown in Figure 1. Only valence electrons were included in the CCSD(T) calculations, i.e. core correlation energy was not included in the calculation of the PECs. The second panel in the figure shows an enlargement of the region of the minima. All results are expressed in kcal/mol with respect to the minimum of each curve, which is independently set to be 0.0 kcal/mol.
FIG. 1. PECs for NaK at different levels of calculation, using the Kalsruhe Def2-QZVPPD basis set. (b) is a close-up of the PECs in (a).

As expected, the Hartree-Fock calculation leads to the erroneous dissociation limit. Post Hartree-Fock methods lead instead to the same correct dissociation limit and the PECs are so close among them as to be nearly indistinguishable. DFT methods exhibit an intermediate behavior between HF and CCSD(T). It does not lead to the correct dissociation limit, but the equilibrium distance is nearer to the post-Hartree-Fock results than to the HF one. Introduction of dispersion using the empirical GD3 correction does not improve the dissociation. On the contrary, it shows a spurious second minimum. This result, not reported earlier to the extent of our knowledge, implies that great care must be exercised in using the GD3 empirical correction in geometry optimizations, PECs or calculation of potential energy surfaces.

Equilibrium distances, dissociation energies, dipole moments and frequencies of the NaK molecule obtained with these methods are shown in Table I. The effect of the basis set on the results was tested only for the PBE0 and CCSD(T,Full) methods (i.e. CCSD(T) method including all valence and core electrons), taking values from the literature and those calculated in this work. Notice that this procedure was applied only for the optimized minimum and not for the other points on the PEC.
TABLE I. Equilibrium bond distances (in Å), dissociation energies (in cm$^{-1}$), dipole moments (in D) and harmonic vibrational frequencies (in cm$^{-1}$) calculated for the NaK molecule using molecular orbital and DFT methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis set</th>
<th>$R_e$</th>
<th>$\Delta E$</th>
<th>$\mu$</th>
<th>$\omega_e$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>Def2-QZVPPD</td>
<td>3.263</td>
<td>12893</td>
<td>6.71</td>
<td>156.6</td>
<td>This work</td>
</tr>
<tr>
<td>PBE0</td>
<td>Def2-QZVPPD</td>
<td>3.549</td>
<td>10768</td>
<td>3.02</td>
<td>123.0</td>
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<tr>
<td>pc-4</td>
<td></td>
<td>3.546</td>
<td>3.01</td>
<td>123.3</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>PBE0-GD3</td>
<td>Def2-QZVPPD</td>
<td>3.571</td>
<td>10767</td>
<td>3.04</td>
<td>118.1</td>
<td>This work</td>
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<tr>
<td>CASSCF</td>
<td>Def2-QZVPPD</td>
<td>3.265</td>
<td>5087</td>
<td>7.39</td>
<td>110.0</td>
<td>This work</td>
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<td>MRCI</td>
<td>Def2-QZVPPD</td>
<td>3.049</td>
<td>5171</td>
<td>3.93</td>
<td>118.6</td>
<td>This work</td>
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<td>CCSD(T)</td>
<td>6-311+G(3df)</td>
<td>3.574</td>
<td></td>
<td></td>
<td></td>
<td>This work</td>
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<tr>
<td>CCSD(T,Full)</td>
<td>Def2-QZVPPD</td>
<td>3.472</td>
<td>5262</td>
<td>3.06</td>
<td>126.7</td>
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<td></td>
<td>Def2-QZVP</td>
<td>3.461</td>
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<td>Def2-TZVP</td>
<td>3.529</td>
<td>3.65</td>
<td>121.1</td>
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<td>This work</td>
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<td></td>
<td>6-311+G(3df)</td>
<td>3.516</td>
<td>3.15</td>
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<td></td>
<td>pc-4</td>
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<td>3.10</td>
<td>122.7</td>
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<td>Aug-pc-2</td>
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<td>Aug-pc-3</td>
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<td>Aug-pc-4</td>
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<td>2.94</td>
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<td></td>
<td>Zemke et al$^a$</td>
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<td></td>
<td>Pseudopotential+extended</td>
<td>3.440</td>
<td>2.76</td>
<td></td>
<td></td>
<td>Aymar &amp; Dulieu$^b$</td>
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<tr>
<td>CASSCF</td>
<td>Pseudopotential+QZ$^c$</td>
<td>3.504</td>
<td>5364</td>
<td>2.68</td>
<td>122.4</td>
<td>Fedorov et al$^d$</td>
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<tr>
<td>Experimental</td>
<td></td>
<td>3.499</td>
<td>5273.62</td>
<td>2.76</td>
<td>124.13</td>
<td>Dagdigian et al$^f$</td>
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$^a$Reference 18.
$^b$Reference 15.
$^c$cc-pCVQZ for Na and small-core relativistic effective core potentials (ECP) of Stuttgart/Cologne group for K.
$^d$Reference 19.
$^e$Reference 14.
$^f$Reference 12.
$^g$Reference 9.

The best results of the equilibrium distance were obtained by Fedorov et al$^9$ using a full CCSDT method (i.e., not using only the perturbative effect of triple excitations). They also obtained good values for the dissociation energy, the dipole moment and the harmonic frequency. Surprisingly, due to the small basis set used, the results of Zemke et al$^{15}$ are also quite good for the equilibrium distance. The dipole moment, however, is much worse than that of by Fedorov et al$^{19}$. We tried to reproduce these results, using the same methodology, but obtained a larger equilibrium distance (3.516 Å with CCSD(T,Full)) and 3.574 Å for CCSD(T)) and dipole moment. The origin of this difference remains unknown. However, it is easy to see that there is a large variation of the results depending on the amount of dynamic correlation included and the size and type of the basis set.
The non-dynamic correlation seems not to be important, as could be expected. It is important to notice that the inclusion of the core relativistic ECP seems to be instrumental for obtaining a better estimation of the dipole moment. Comparing the calculations by Zemke et al (without pseudopotentials) with those of Aymar and Dulieu (which resort to the pseudopotential) it can be seen that even if the equilibrium distance is similar, the dipole moment is much improved. This is not a rigorous proof, because also the basis set in the calculations by Aymar and Dulieu is larger. However, our best calculation, CCSD(T)/aug-cc-pc4, reproduces very well the equilibrium distance (-0.4% error) and the harmonic vibrational frequency (1.3% error) but exhibits a 13% error in the dipole moment. It may be concluded, at least until further calculations, that the dipole moment is influenced by core relativistic effects on K.

It is important to realize the effect that the inclusion of core electrons have in CCSD(T) calculations. Considering only the 6-311+G(3df) and Def2-QZVPDD basis sets, one can observe important variations between the CCSD(T,Full) and CCSD(T) calculations. In both cases, the too large bond distances obtained with CCSD(T), 3.574 and 3.665 Å respectively, decrease to the much better 3.516 and 3.472 Å when all electrons are correlated in the CCSD(T) calculations.

The increase of the basis set from Def2-TZPV to Def2-QZPVDD produces a shorter equilibrium distance and, more important, a decrease of the dipole moment of 0.6 D, nearer to the experimental result. The balance between polarization and diffuse functions seems to be extremely important to obtain this result, and the progression of the results in the series of correlation consistent basis sets Aug-pc-0, (9s8p)/(6s4p), to Aug-pc-4, (25s17p9d3f2g)/(9s7p6d3f2g), supports this assertion. Up to aug-pc-2, the equilibrium distance decreases, approaching the experimental value, and so does the dipole moment. However, the equilibrium distance obtained with the aug-pc-3 and aug-pc-4 basis sets is too short and the dipole moment bounces back, becoming again larger than 3 D. In our opinion, the good results reported for the dipole moment at the CCSD(T) and CCSDT levels is mostly due to error compensation within the basis sets and pseudopontials used. In particular, there is a strong suggestion that core relativistic effects in K seem to be necessary to describe weel the dipole momento, as discussed before. No convincing evidence exists as yet that the experimental dipole moment can be well predicted using a complete basis set extrapolation scheme.

B. Results obtained using QMC methods.

The potential energy curves obtained using DMC with trial functions built at different theoretical levels and optimized using VMC are shown in Figure 2. Ross experimental curve is included by way of comparison. Error bars are included at each point.
FIG. 2. PECs calculated using DMC method with a VQC/ANO basis set. The experimental curve of Ross is included as a comparison. (b) is a close-up of (a) in the region of the minima. Error bars are shown.

Several curves are presented in this figure. The basic calculation is the 2-body Jastrow corrected Hartree-Fock trial function, which we called simply HF. To that, one can add improvements like CISD, CASSCF and SOCI/CASSCF as shown in the figure. As expected, introducing dynamical correlation energy corrects the form of the QMC(HF) curve. The QMC(CISD) approximate the experimental dissociation curve. Comparing the experimental curve with those obtained by QMC, one sees a very reasonable agreement that does not depend greatly on the trial wavefunction used. Nonetheless, the dissociation energy does depend on the method used, as can be seen in Table II.

TABLE II. Equilibrium distances (in Å) and dissociation energies (in cm$^{-1}$) calculated using different methods, trial functions and correction factors. Errors reported in Å and cm$^{-1}$

<table>
<thead>
<tr>
<th>Method</th>
<th>Trial function</th>
<th>Basis Set</th>
<th>Correction</th>
<th>$r_e$</th>
<th>$\Delta E$</th>
<th>Statistical Error</th>
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<tr>
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<td>Jastrow</td>
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<tr>
<td>B3LYP</td>
<td>Jastrow</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>HF</td>
<td>VQC/ANO</td>
<td>Jastrow</td>
<td>3.51</td>
<td>0.10</td>
<td>5515</td>
<td>500</td>
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<tr>
<td>CISD</td>
<td>VQC/ANO</td>
<td>Jastrow</td>
<td>3.47</td>
<td>0.06</td>
<td>5264</td>
<td>420</td>
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<tr>
<td>CASSCF</td>
<td>VQC/ANO</td>
<td>Jastrow</td>
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<td>0.04</td>
<td>5582</td>
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<td>SOCI/CASSCF</td>
<td>VQC/ANO</td>
<td>Jastrow</td>
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<td>TZV</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>CCSD(T)$^a$</td>
<td>Def2-QZVPPD</td>
<td></td>
<td>3.472</td>
<td></td>
<td>5262</td>
<td></td>
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<tr>
<td>Experimental$^b$</td>
<td></td>
<td></td>
<td>3.499</td>
<td></td>
<td>5273.62</td>
<td></td>
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</tbody>
</table>

$^a$Reference 14.

$^b$Result obtained by conventional MO calculations with the CCSD(T) method and the Def2-QZVPPD basis set, as reported in Table I.
The equilibrium distances and dissociation energies were estimated by fitting a Morse potential to each curve, adjusting the parameters using a $\chi^2$-fitting procedure. The error bars were calculated as $\pm 2\sigma$ to be within the 95% confidence interval.

The values obtained with DFT trial wavefunctions are about $400 \text{ cm}^{-1}$ smaller than the experimental one. The HF trial wavefunction, on the other side, gives a value which is closer to experiment, but about $250 \text{ cm}^{-1}$ above it. Dynamical and non-dynamical correlation effects work somewhat in opposite directions. Including the first using CISD makes the results quite close to experiment, but when non-dynamical correlation effects are included through CASSCF, the dissociation energy is again overestimated. The SOCI/CASSCF method corrects the equilibrium distance, but makes the dissociation energy even worse.

The origin of the remaining error is not clear. One problem may be the use of the pseudopotential. As the conventional CCSD(T) calculations show, the influence of the core correlation energy is important. Perhaps the remaining error is then due to the ECP and/or the use of a not so large basis sets. It must be noted that the error bars at the 95% confidence level for the HF and CISD calculations are significative larger than with others wavefunctions. A possible explanation of why the conventional methods give a better dissociation energy may be that some error cancellation is built into the optimized basis sets. Since DMC can not rely on this mechanisms, as its correlation treatment is not constrained by a basis set, this could be a possible origin of the discrepancy. More research is needed to assess this point more accurately.

Expectation values of quantities which commute with the Hamiltonian are exact in DMC. However, expectation values of non-commuting operators, are estimated by mixed estimators and therefore are not exact. Thus DMC has problems to predict dipole moments. This drawback can be corrected using an approximate pure estimator ($2 D_{\text{dmc}} - D_{\text{vmc}}$), as mentioned in note b ,Table III or using RMC, which is what we employed in this work with several trial wavefunctions. Due to the difficulty of the calculations, only the HF and DFT trial functions were used.

The dipole results obtained using the RMC methodology have good accuracy but not enough precision even when the simulations steps or reptile lengths were increased. In all cases values are quite close to experimental one, but with a significant error bar (at 95% level of confidence), as shown in Table III. Contrariwise, the corrected DMC values are more precise but less accurate, except in the case of the Hartree-Fock wavefunction.

Two interesting comparisons can be performed to assess the precision and accuracy of these calculations. On the one side, one can compare DMC and RMC values with the different trial functions (see later on the technical details on the way the RMC values of the dipole moment were calculated). The results show that the RMC results are always closer to the
experimental value (see Table III). This, up to our knowledge, is one of the very few examples in the literature of a comparison of DMC and RMC values for dipole moments, where the advantage of RMC is clearly shown. In this respect, it must be mentioned the work of Wagner and Mitas\textsuperscript{47} where they calculated dipole moments of transition metal monoxides and pointed out that the dipole moment remains an extraordinary sensitive quantity that is a stringent test for theory. In a similar work using DMC Guo \textit{et al.}\textsuperscript{45} studied the dipole moment of both LiSr and KRb and found reasonable agreement in the second case, but not the first (about half the value predicted by conventional methods). RMC seems to be helpful in solving this problem.

We followed the work of Rothstein\textsuperscript{45} who performed RMC calculations using the B3LYP wavefunction and analyzing the convergence of energy and dipole moment using different time steps and reptile size. We used six values for the reptile size (24, 32, 40, 48, 64, 80) and, for each value, we varied the time step and number of beads so that the former was kept constant. We chose the values of 0.0025, 0.0050, 0.0075, 0.0100, 0.0150 and 0.0200 for the time step. The energy of the system converged for all sizes of the reptile. However, the dipole moment converged only for the largest sizes. Meaningful data were obtained for 80 Hartree\textsuperscript{1} and for this time step five independent calculations were run. The average value of these runs yielded a zero time-step extrapolation of 2.6(2) D. This value is shown in Table III together with our own values obtained with other methodologies and the experimental one.

<table>
<thead>
<tr>
<th>Method</th>
<th>Trial function (basis set)\textsuperscript{a}</th>
<th>Dipole moment (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMC\textsuperscript{b}</td>
<td>HF(SJ)</td>
<td>1.6 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>PBE(SJ)</td>
<td>2.8 ± 0.2</td>
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<td></td>
<td>B3LYP(SJ)</td>
<td>3.1 ± 0.2</td>
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<td>RMC</td>
<td>HF(SJ)</td>
<td>2.7 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>PBE(SJ)</td>
<td>2.6 ± 0.4</td>
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<tr>
<td></td>
<td>B3LYP(SJ)</td>
<td>2.6 ± 0.4</td>
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<tr>
<td>HF</td>
<td>Def2-QZVPPD</td>
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<td>MRCI</td>
<td>Def2-QZVPPD</td>
<td>3.93</td>
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<td>CCSD(T)</td>
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<td></td>
<td>Aug-cc-p4</td>
<td>3.11</td>
</tr>
<tr>
<td>Experimental\textsuperscript{b}</td>
<td></td>
<td>2.76 ± 0.05</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Trial function applies for MC calculations; basis set applies to conventional DFT or MO calculations

\textsuperscript{b}The linear correction in DMC (extrapolated estimator = 2 DMC - VMC) was used to reduce the DMC bias due to the non locality of the dipole operator.

\textsuperscript{c}Reference \textsuperscript{12}.

While there is a big difference between the DMC results using several trial wavefunctions, the RMC results have a smaller dispersion. Both the RMC/HF 2.7D and RMC/B3LYP 2.6 D calculations afford results that encompass the...
experimental value. Both values are even better that the CCSD(T) result with the most extended basis set performed in this paper. We already mentioned that better results shown in the literature using CCSD(T) exhibit error compensation between the method and the pseudopotential included in the basis set. Even when using a very simple trial wavefunction, as Hartree-Fock, both DMC and RMC results are better than simple conventional HF calculations.

It is interesting to notice that even when the dipole moments calculated at the DMC level are quite sensitive to the trial wavefunction, this is not the case for the RMC calculations, at least with the functionals we used in this work. Regretfully, the error bars are significantly larger than those of DMC although in all cases the experimental result is included in the error interval. RMC results are significantly better than those obtained from MO methods.

The second comparison that can be done refers to the known problem of ergodicity in RMC. Due to the algorithms used, it is possible for the reptiles to bounce back and forth without changing the electron coordinates of the central bead (as described in the QMCPack code manual). Thus, strong autocorrelation effects may be occurring, and this effect should be checked. We actually found that these effects were present in our calculations. To reduce them as much as possible we increase the sampling period used in the reblocking method. Thus, the procedure consisted in calculating the average from more spaced configurations when the time step between configurations decreased. This procedure provided the necessary decorrelation of the averages.

IV. CONCLUSIONS

Quantum Monte Carlo calculations of the equilibrium distance, dissociation energy and dipole moment of NaK have been performed using both DMC and RMC methods. CCSD(T) calculations, as well as CASSCF and MRCI, using several basis sets were performed to use as a comparison. It was found that the dipole moment of NaK is very sensitive to the size and composition of the basis set. No systematic trend was found in the results obtained, even if progressively larger and more complete basis sets were used. Good results obtained in other calculations seem to be an effect of error compensation between the method, the basis set and the use of pseudopotentials.

The QMC results obtained showed that the dissociation energy was overestimated when a HF trial function was employed. Use of a CISD wavefunction built on top of the HF wavefunction lead instead to quite good of the result. The use of a SOCI/CASSCF trial wavefunction did not afford any improvement in the results. The dissociation energies obtained with conventional MO methods are better than those obtained with QMC. Whether this disagreement can be corrected by use of larger basis sets, better trial wavefunctions or longer times is a matter of speculation. Moreover, the use of the Burkatski
Filippi Dolg ECP means that only one electron is preserved in the description of Na. Thus, one can not rule out that the error may be in the use of the ECP.

On the contrary, the dipole moment obtained using the RMC method with as simple a trial wavefunction as HF is as good as the value obtained with the best CCSD(T) calculation performed in this paper. Nonetheless, it is worse than the values obtained using core pseudopotentials and valence only basis sets. These results, however, can not be systematically improved, while the QMC can be better if longer simulations or better trial wavefunctions are used. Actually, all RMC dipole estimation done in this paper are well in agreement among themselves and with the experimental value, exhibiting a better behaviour than the other methods tested.

ACKNOWLEDGMENTS

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