The Generalized Relativistic Effective Core Potential Calculations of the Adiabatic Potential Curve and Spectroscopic Constants for the Ground Electronic State of the Ca$_2$

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Abstract

The potential curve, dissociation energy, equilibrium internuclear distance, and spectroscopic constants for the $^1\Sigma_g^+$ ground state of the Ca$_2$ molecule are calculated with the help of the generalized relativistic effective core potential method which allows one to exclude the inner core electrons from the calculations and to take the relativistic effects into account effectively. Extensive generalized correlation basis sets were constructed and employed. The scalar relativistic coupled cluster method with corrections for high-order cluster amplitudes is used for the correlation treatment. The obtained results are analyzed and compared with the experimental data and corresponding all-electron results.

SHORT NAME: GRECP calculations of Ca$_2$

Key words: calcium dimer, van der Waals interactions, generalized relativistic effective core potential method, scalar-relativistic correlation calculations, spectroscopic constants

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I. INTRODUCTION.

Recently we have reported calculations of the potential curve, dissociation energy, equilibrium internuclear distance, and spectroscopic constants for the ground state of the Yb\(_2\) molecule [1]. To estimate reliably the computational accuracy, one has to analyze carefully the errors of all the used approximations. A direct way to calculate these errors is to carry out the calculations both with and without a given approximation. As a rule, this way is impractical because the approximations are normally introduced just to make the computations feasible. An alternative way is to compare the calculated results with the corresponding experimental data. However, the experimental data are not always accessible or have relatively large errors as is in the case of Yb\(_2\). One can then perform the calculations on the well-studied system with similar electronic structure within the same approximations having in mind a reasonable suggestion that the errors for similar systems will be close to each other. As an appropriate analog of Yb\(_2\), we have chosen the Ca\(_2\) molecule that was studied in details both experimentally [2–5] and theoretically [6–17].

Similar ground states with the closed-shell (\(ns^2\)) valence configuration and similar first excited \(ns^1np^1(3P_0, 3P_1, 3P_2)\) terms are observed for the Ca (\(n = 4\)) and Yb (\(n = 6\)) atoms [18]. These atoms also have similar \((n - 1)s^2(n - 1)p^6\) outercore and lowest-lying \((n - 1)d^0\) virtual shells. The main differences are the presence of the closed 4\(f^{14}\) outercore (or subvalence) shell and notably stronger relativistic effects in Yb. However, the contribution from “unfreezing” the 4\(f\) shell to the binding energy is rather small (about 3%). This can be easily understood because the 4\(f\) shell has a significantly smaller radius and essentially lower orbital energy than those for 6\(s\) (and 6\(p\)) ones.

The experimental investigations [2–5, 19] of Ca\(_2\) were motivated by considerable interest in understanding the van-der-Waals interactions, interpretation of stellar absorption spectra, studying the metal vapor excimer laser systems, prediction on cold collision phenomena, etc. Several fields in ultracold atom physics such as photoassociation [20, 21], optical frequency standards [22, 23] and possible Bose-Einstein condensates [24, 25] have been initiated during the last decade with magneto-optical traps [20, 26]. Interatomic interaction potentials are required for these investigations. The theoretical studies are additionally aimed to test the modern quantum chemical methods for this computationally difficult system (multiconfigurational nature of the ground state, weak van-der-Waals interaction, noticeable relativistic
corrections). Some of the above cited authors \[13, 16\] carried out all-electron (AE) molecular calculations with the help of the same correlation method as in the present paper that allows us to estimate the accuracy of the more economical generalized relativistic effective core potential (GRECP) method in reproducing the all-electron molecular results.

This paper presents the results of our calculations on the dissociation energy, equilibrium internuclear distance and spectroscopic constants for the Ca\(_2\) molecule using the GRECP method, extremely flexible generalized correlation basis sets, correlation treatment by the coupled cluster method with single, double and non-iterative-triple cluster amplitudes (CCSD(T)) and contributions from higher-order cluster amplitudes in comparison with the experimental data and corresponding all-electron results.

II. CALCULATIONS AND DISCUSSION.

Scalar relativistic calculations were performed within the GRECP model \[27, 30\] using the CCSD(T) method (implemented in the MOLCAS program package \[31\]) for correlation treatment. The 4s shell of the Ca atom is usually considered as the valence one. The 3s and 3p shells were considered as the outercore ones in the GRECP generation procedure \[27\]. Thus, we use the GRECP with 10 explicitly treated electrons for each Ca atom. In a series of preliminary calculations, we have estimated the contributions from correlations with different shells of Ca to the dissociation energy of Ca\(_2\) (some of them are presented in Table \[II\]). The main contribution is provided by the 4s shell whereas the contributions from the 3s and 3p shells are relatively small. This enabled us to “freeze” 3s, 3p shells in the starting set of calculations marked as “4e” and to incorporate other correlation effects through appropriate corrections. It is clear that the corresponding contributions from the innermore 2p, 2s, and 1s shells will be significantly smaller so that their complete exclusion from the correlation treatment within the GRECP model seems to be well justified. Generalized correlation basis sets comprising \((22, 22, 21, 6, 4, 4, 1)/[10, 8, 9, 6, 4, 4, 1]\) functions, basis set C (core), in the former and \((12, 13, 9, 6, 3, 3, 2)/[12, 13, 9, 6, 3, 3, 2]\), basis set L (large), \((12, 13, 9, 6, 3)/[4, 4, 4, 1, 1]\), basis set M (medium, with the \(h\) and \(i\) harmonics removed from the previous uncontracted basis set), in the latter cases were constructed by the procedure developed previously \[32, 33\]. For the basis set C construction, the large number of the states of the Ca atom and its cation, the leading configurations of which differ by the occupation
numbers of the 3\textit{d}, 4\textit{s}, 4\textit{p} valence spinors and have the completely occupied 3\textit{s}, 3\textit{p} outer core spinors, were considered. The basis set construction procedure is designed to account primarily for correlations which have different contributions to the states under consideration, so that possible omissions in the resulting basis set cause nearly state-independent errors and give accurate transition energies. Therefore, the resulting basis set may be nearly complete in the valence region but relatively poor in the outer core region. The basis set superposition errors (BSSE) will have weak dependence on the valence shell configuration, and may be estimated quite accurately by the counterpoise correction (CPC) method because there are no ambiguities in the occupation numbers for the outer core shells in the effective state of “atom-in-molecule”.

Calculations were carried out for the internuclear distances (\(R\)) presented in Table I (from 6 to 13 a.u. and for 100 a.u.). All our results were rectified using the CPC \[34, 35\] calculated for the Ca 4\textit{s}\(^2\) state with one more Ca atom treated as a ghost one. The stage of calculation of the molecular constants \[36\] begins with fitting the numerical potential curve for the dimer by polynomials with the help of the quasi-Hermitian method. Appropriate derivatives of the potential curve at the equilibrium point are calculated by recurrence relations. Then rovibrational Schrödinger equation is solved by the Dunham method to express the Dunham coefficients in terms of these derivatives.

The \(^1\Sigma^+_g\) closed-shell ground state of the Ca\(_2\) molecule dissociates into two Ca atoms in the 4\textit{s}\(^2\)(\(^1\text{S}\)) ground state. The computed ground-state potential energy curves for the Ca\(_2\) molecule are shown in Table I and Figure I. One can see from Figure I that our final potential curve is in a good agreement with the experimentally derived curves in papers \[2, 3, 5\]. Our results for the dissociation energy, equilibrium internuclear distance, and main spectroscopic constants are listed in Table II. Following the scheme of our previous Yb\(_2\) calculation \[1\], we started from 4-electron scalar relativistic CCSD(T) (denoted as 4e-CCSD(T) below) calculations with rather large basis set L, which gave \(D_e = 1022\) cm\(^{-1}\) (that is about 1.5 times larger than that for Yb\(_2\)). The negligible CPC (0.3 cm\(^{-1}\) for dissociation energy) indicates a good quality of the basis set used. Subsequent calculations of the effects of the difference between the iterative and non-iterative triple cluster amplitudes (CCSDT-CCSD(T) or contribution from iteration of triples) as well as of quadruple cluster amplitudes (these two contributions are denoted further as the iTQ contribution), and valence – outer core correlations (OC) described below have shown that the corresponding contributions to
the Ca–Ca interaction energy are within 17% (with respect to our final dissociation energy of 1136 cm\(^{-1}\)), thus, justifying the choice of the 4e-CCSD(T) scheme as a good initial approximation. Note that the 4-electron FCI or 20-electron CCSD(T) calculations with considerably smaller basis sets M or C have given essentially lower \(D_e\) estimates (\(D_e = 959\) or 930 cm\(^{-1}\), correspondingly). Thus, the quality of the basis set is important for accurate calculations of the calcium dimer.

The contribution from the quadruple cluster amplitudes together with the difference between the iterative and non-iterative triple amplitudes, \(\Delta E_{iTQ}\), was estimated as the difference between the energy lowerings \(E = \mathcal{E}(Ca_2) - 2\mathcal{E}(Ca)\) obtained in the 4e-FCI and 4e-CCSD(T) calculations with basis set M for each of the above mentioned internuclear distances

\[
\Delta E_{4e- iTQ}^M(R) = E_{4e- FCI}^M(R) - E_{4e- CCSD(T)}^M(R),
\]

where \(\mathcal{E}(Ca_2)\) and \(\mathcal{E}(Ca)\) are the total energies calculated in the molecular basis set for the Ca\(_2\) molecule and the Ca atom, respectively. Thus, this contribution takes into account the CPC. This difference was then added to the total energy obtained in the 4e-CCSD(T) calculation with basis set L

\[
E_{4e-CCSD(T)+iTQ}(R) = E_{4e-CCSD(T)}^L(R) + \Delta E_{4e- iTQ}^M(R).
\]

The dissociation energy, equilibrium internuclear distance, and spectroscopic constants were calculated with the obtained 4e-CCSD(T)+iTQ potential curve. The derived correction from the iTQ amplitudes to the dissociation energy, 190 cm\(^{-1}\), is 17% with respect to our final \(D_e\) value (that is also about 1.5 times larger by absolute value than that for Yb\(_2\) but has the same relative value).

The contribution from the correlations with the 3s and 3p electrons, \(\Delta E_{OC}\), was estimated as the difference between the energy lowerings found in the 20e-CCSD(T) and 4e-CCSD(T) calculations with basis set C for each of the above mentioned internuclear distances

\[
\Delta E_{OC}^{CCSD(T)}(R) = E_{20e-CCSD(T)}^C(R) - E_{4e-CCSD(T)}^C(R).
\]

The only difference between these two calculations is the number of correlated electrons, therefore, the differences in the energy lowerings give the contribution of the OC correlations. These differences were then added to the 4e-CCSD(T) and 4e-CCSD(T)+iTQ energy
lowerings derived above:

\begin{align*}
E_{4e-CCSD(T)+OC}(R) &= E_{4e-CCSD(T)}^L(R) + \Delta E_{OC}^{CCSD(T)}(R), \\
E_{4e-CCSD(T)+iTQ+OC}(R) &= E_{4e-CCSD(T)+iTQ}(R) + \Delta E_{OC}^{CCSD(T)}(R).
\end{align*}

The 4e-CCSD(T)+OC and 4e-CCSD(T)+iTQ+OC dissociation energy, equilibrium internuclear distance and spectroscopic constants were calculated with the obtained potential curves. The dissociation energy was decreased by 76 cm\(^{-1}\) (that is about 1.4 times larger than that for Yb\(_2\)), whereas the corresponding CPC contribution was obtained as about 10 cm\(^{-1}\).

It should be noted that the contribution from the spin-dependent interactions for the excluded innercore 2p shell of Ca is effectively taken into account by the GRECP method. The contribution from the spin-dependent interactions for the outercore, valence and virtual shells of Ca is neglected in the present scalar relativistic calculations. We estimated this contribution as the difference between the energy lowering in the 20e-CCSD calculations with the full spin-dependent and spin-averaged GRECP operators \(^{27}\) with the \((22, 22, 21, 6)/[5, 4, 3, 2]\) basis set for the internuclear distance \(R=8.0\) a.u. (that is close to the equilibrium one). The CPC was also taken into account. The contribution was significantly less than one wave number.

It should be noted that the low convergence threshold of \(10^{-8}\) and the approximation of the potential curve by analytic polynomials were used. The errors in the calculated total energies have rather systematic nature (due to neglecting the unaccounted effects) than a random one, therefore, the large number of points is not necessary for good statistics. To check the saturation in the number of the potential curve points, we have repeated the dissociation energy, equilibrium internuclear distance and spectroscopic constant calculations without two extreme points (corresponding to 6 and 13 a.u.). As one can see from Table \(\text{II}\) the given data are almost unchanged. Similar situation was observed for different analytical functions (Legendre, second kind Chebyshev and power polynomials) used for interpolation in program \(^{36}\) instead of the Laguerre polynomials. The latters provided the best approximation in the least square sense and were used for the calculation of the data in Table \(\text{II}\).

If the same correlation method and basis sets of similar flexibility are used, one can compare the GRECP and all-electron results. The nonrelativistic AE/CCSD(T) dissociation
energies extrapolated to the complete basis set limit and with accounting for the CPC were calculated in \([13, 16]\) as 993 and 997 cm\(^{-1}\). The relativistic effects are taken into account in the GRECP method by construction. Moreover, interplay of the relativistic and correlation effects is also taken into account in the correlation GRECP calculations. The relativistic effects were added as corrections in \([13, 16]\). They decreased the dissociation energy on 37 cm\(^{-1}\) in the both above studies. Thus, our 4e-CCSD(T)+OC dissociation energy of 939 cm\(^{-1}\) is in a good agreement with the corrected 956 and 960 values from the above all-electron calculations. It should be noted that this GRECP result was obtained with rather large but a finite basis set without the complete basis set limit extrapolation. The all-electron dissociation energies calculated in \([13, 16]\) with the largest basis sets and CPCs (but without the extrapolation to the complete basis set limit) are by 10 and 41 cm\(^{-1}\) lower. We conclude that the small difference (about 20 cm\(^{-1}\)) in the GRECP and all-electron results can be mainly due to both the GRECP errors and incompleteness of our basis set. The approximate accounting for the relativistic effects in \([13, 16]\) can also contribute to this difference. This difference is significantly smaller than the unaccounted iTQ contribution for the OC shells. We estimated the iT contribution for the OC shells with the help of the 20e-CCSDT (i.e. with the iterative triple amplitudes), 20e-CCSD(T) 4e-CCSDT, and 4e-CCSD(T) calculations with the \((22, 22, 21, 6)/(5, 4, 3, 2)\) basis set for the internuclear distance \(R=8.0\) a.u. as

\[\Delta E_{iT&OC}(R) = E_{20e-CCSDT}(R) - E_{20e-CCSD(T)}(R) - E_{4e-CCSDT}(R) + E_{4e-CCSD(T)}(R),\]

The CPC was also taken into account. This contribution decreased the dissociation energy by -101 cm\(^{-1}\). These dissociation energies differ from the final ones by the iTQ contribution which were calculated as 197 and 196 cm\(^{-1}\) in the present paper and in \([13]\) only for the valence shells and as 136 cm\(^{-1}\) in \([16]\) for both the valence and outercore shells but without the CPC.

III. CONCLUSIONS.

One can see that the GRECP method allows one to reproduce perfectly the corresponding all-electron results from \([13, 16]\). Our final results are presented in the 4e-CCSD(T)+iTQ+OC line in Table III. The very small differences between these results and
the experimental data are mainly due to neglecting the iTQ contribution for the OC shells which will decrease the dissociation energy. The errors due to the incompleteness of our basis sets and the errors of the GRECP method are expected to be essentially smaller. A good agreement of our results with the experimental data should not be considered as fortuitous coincidence because it is observed not only for one parameter (such as $D_e$) but also for several independent parameters ($R_e, D_e, w_e, w_e x_e, \alpha_e, -Y_{02}$).

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TABLE I: Potential energy functions for the Ca$_2$ ground state calculated with the help of the GRECP and different correlation methods. Internuclear distances $R$ and total energy lowerings $E = \mathcal{E}(Ca_2) - 2\mathcal{E}(Ca)$ are in a.u.

| $R$ | $E(R)$ from 4e-CCSD(T)+OC+iTQ+iTQ | +OC+iTQ+iTQ |
|-----|----------------------------------|-------------|
| 6.0 | 0.02033301 0.02378395 0.01875840 |             |
| 6.5 | 0.00663326 0.00778011 0.00523450 |             |
| 7.0 | -0.00026847 -0.00049810 -0.00151446 |         |
| 7.5 | -0.00327505 -0.00421945 -0.00437114 |         |
| 8.0 | -0.00421751 -0.00543463 -0.00516116 |         |
| 8.5 | -0.00416952 -0.00539711 -0.00496276 |         |
| 9.0 | -0.00371447 -0.00482274 -0.00436746 |         |
| 10.0| -0.00258660 -0.00336334 -0.00301022 |         |
| 11.0| -0.00167843 -0.00218223 -0.00194408 |         |
| 12.0| -0.00105967 -0.00137987 -0.00122368 |         |
| 13.0| -0.00066214 -0.00086506 -0.00076319 |         |
| 100.0| 0.00000000 0.00000000 0.00000000 |         |
TABLE II: The dissociation energy, equilibrium internuclear distance, and spectroscopic constants of the $^1\Sigma_g^+$ ground state of the $^{40}\text{Ca}_2$ molecule. $R_e$ is in Å, $B_e$ in $10^{-2}$ cm$^{-1}$, $\alpha_e$ in $10^{-4}$ cm$^{-1}$, $Y_{02}$ in $10^{-8}$ cm$^{-1}$, and other values in cm$^{-1}$.

| Method | $R_e$  | $D_e$  | $w_e$  | $D_0^e$ | $B_e$  | $w_e\alpha_e$ | $\alpha_e$ | $-Y_{02}$ |
|--------|--------|--------|--------|---------|--------|---------------|------------|----------|
| Present GRECP calculations: |
| 4e-CCSD(T) | 4.394 1022 | 62.5 991 | 4.36 1.05 | 6.88 | 8.48 |
| 4e-CCSD(T)+OC | 4.337 939 | 60.1 909 | 4.47 1.06 | 7.59 | 9.95 |
| 4e-CCSD(T)+iTQ | 4.345 1212 | 67.4 1178 | 4.46 1.01 | 6.37 | 7.79 |
| 4e-CCSD(T)+iTQ+OC | 4.283 1136 | 65.4 1104 | 4.59 1.02 | 6.97 | 9.03 |
| $-^a$ (2 less points) $^a$ | 4.283 1136 | 65.4 1104 | 4.59 1.03 | 6.98 | 9.03 |
| Experimental data: |
| Balfour, 1975 [2] | 4.277 1075±150 | 64.9 1043 | 4.61 1.07 | 7.03±0.03 | 9.52±0.11 |
| Vidal, 1980 [3] | 4.279 1095 | 65.0 1063 | 4.61 1.08 | 6.97 | 9.07±0.11 |
| Bondybey, 1984 [4] | 1095 | 65.1 1063 | 4.61 | 6.97 |
| Allard, 2002 [5] | 1102 | 1070 |
| Previous calculations: |
| 2e-PP/4e-FCI [6] | 5.1 | 234 |
| 2e-PP/4e-MRCI+QDPT [14] | 4.29 | 943 | 61.7 912 | 0.8 |
| AE/20e-CCSD(T) [9] | 4.326 991 | 61.5 961 | 1.07 |
| 10e-PP/20e-CCSD(T) [10] | 4.37 | 1015 | 62.4 984 |
| AE/CCSD(T) [15] | 4.299 1034 | 90.0 989 |
| AE+DPT2/20e-CCSD(T)+iT+(Q) [16] | 4.287 1095 | 63.8 1063 | 4.58 1.15 | 7.23 |
| AE+BP/SAPT [11] | 4.3 | 1113 | 1082 |
| AE+DK/CCSD(T)+iTQ [13] | 1152±51 |
| AE/4e-ICF [7] | 4.342 1240 | 67.9 1206 | 1.06 |
| AE/4e-CCSDT-1a+d [17] | 4.297 1277 | 75.7 1239 |

$^a$The 4e-CCSD(T)+iTQ+OC calculation only for 9 internuclear distances ($R$) from 6.5 to 12 a.u. (and for 100 a.u.) which are presented in Table II.
FIG. 1: The calculated (4e-CCSD(T)+iTQ+OC) and experimentally derived (Balfour, 1975 [2]; Vidal, 1980 [3]; Allard, 2002 [5]) potential energy functions for the Ca$_2$ ground state.