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A note on the electronic structure of O_2^-

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Summary. The electronic spectrum of O_2^- is reinvestigated using CASSCF and CI methods. In particular, a previously noted curious flattening of the $A^2\Pi_u$ curve has been studied in detail. The present analysis disagrees with the previous one where this flattening was found to be a result of an avoided curve crossing between a valence and a Rydberg state of O_2^-. A simple procedure is suggested to determine whether a wavefunction is of real Rydberg character or if the bound character of the state is just an artefact of the calculation.

Key words: Gas phase O_2^- – Electronic structure – Rydberg states

1. Introduction

In the theoretical modelling of adsorbates on surfaces it is often of interest to make comparisons to similar gas phase molecules. Through the recent experiments on photodesorption and photodissociation of O_2 adsorbed on Pd(111) [1] and Pt(111) [2] we became interested in the electronic spectrum of gas phase O_2^-. A possible similarity between the spectrum of chemisorbed O_2 and that of gas phase O_2^- is not unlikely since chemisorbed O_2 becomes negatively charged by about one unit on most metal surfaces [3]. There have been only four theoretical studies on the spectrum of O_2^-, of which the most recent one is 10 years old. The first one of these is a preliminary report by Michels and Harris [4]. The second one is a CI and MCSCF study by Krauss et al. [5]. The main result of that study is that all the excited states of O_2^- have internuclear separations at least 1 a_0 longer than the ground state. The two lowest states, the $a^4\Sigma_u^-$ and $A^2\Pi_u$, were characterized as shape and valence Feshbach resonances, respectively. Five years later this work was continued by Das et al. [6], and more accurate MCSCF

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calculations on the lowest four states were reported. Already in that study, a curious flattening of the inner part of the $A^2\Pi_u$ state was shown in a figure. This flattening was then the sole subject of an additional report by Das et al. [7], who concluded that the unusual shape of the potential curve for this state was a result of a curve crossing between a valence and a Rydberg state. They further noted that this region of the potential curve differed sharply from the one reported by Michels and Harris. The new shape of the $A^2\Pi_u$ state was used by Das et al. to explain results from an electron scattering experiment on O_2 and was also shown to be in better agreement with the experimentally deduced curve for this state of O_2^-. Since this potential curve could be of interest in the interpretation of the photostimulated processes occurring on metal surfaces, and since all previous theoretical calculations are fairly old we decided to make a reinvestigation of this state at the CI level. It turns out that the results of our study do not agree with those of Das et al. The reason for this disagreement is the subject of this note.

2. Computational details

Calculations including electron correlation were performed for the potential curves of the lowest states of O_2^- with emphasis on the $A^2\Pi_u$ state. The basis set for oxygen was the Dunning [4*s*,3*p*]-set [8] with a single *d*-function with exponent 1.0 added. Since the $A^2\Pi_u$ potential curve was found by Das et al. [7] to have a curve crossing between a valence state and a Rydberg state, diffuse *p*-functions were also added to the basis set. In the first set of calculations, to be described below, a single diffuse *p*-function was added. In subsequent calculations the description of the diffuse region of the wavefunction was improved by extending the diffuse *p*-set to three uncontracted functions. The MCSCF calculations were performed using the CASSCF procedure [9] with active spaces allowing for proper dissociation. When the full potential curves were generated for both the $X^2\Pi_g$ and the $A^2\Pi_u$ states, the active orbital space simply included the molecular orbitals formed from the atomic 2*p* orbitals. These orbitals are the $3\sigma_g$, $3\sigma_u$, $1\pi_u$ and $1\pi_g$ orbitals. The orbitals obtained from the atomic 1*s* and 2*s* orbitals were thus inactive. When the inner part of the $A^2\Pi_u$ curve was investigated further, an additional π_u orbital was added to the active space to allow for a proper description of the curve crossing region. In the subsequent multi-reference CI calculations the externally contracted CI (CCI) method [10] was used and all the configurations with coefficients greater than 0.05 were selected as reference states.

3. Results and discussion

The ground state of the O_2 molecule has the occupation $3\sigma_g^2 1\pi_u^4 1\pi_g^2$ with an overall coupling to $^3\Sigma_g^-$. When an electron is added it naturally goes into the half empty $1\pi_g$ orbital leading to a $^2\Pi_g$ ground state for O_2^-. The lowest valence excited state is obtained by moving an electron from $1\pi_u$ to $1\pi_g$ leading to a $^2\Pi_u$ state which is the focus of interest in this study.

The first set of calculations on O_2^- were made with one diffuse *p*-function with exponent 0.059667 (even-tempered from the Dunning *p*-basis). The resulting potential curves for the two lowest states are shown in Fig. 1 together with the corresponding results obtained by Das et al. [6, 7]. To be comparable, the

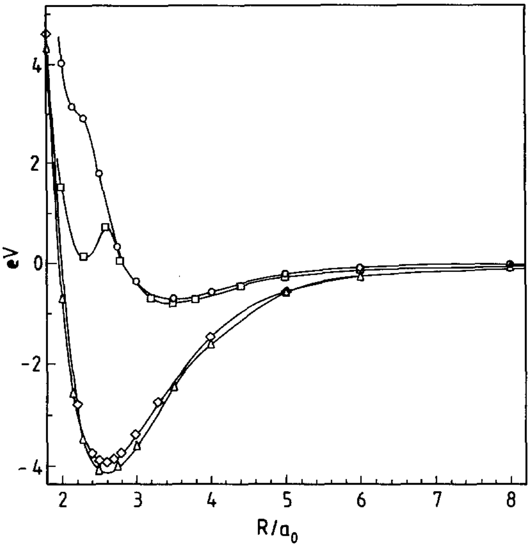

Fig. 1. Potential curves for $O_2^- X^2\Pi_g$ and $A^2\Pi_u$ as calculated in this work (◇,□) and [7] (△,○)

curves from our calculations and the ones from [6, 7] have been drawn to have the same asymptote for the ground state. We first note that the results of the two calculations for both the ground $X^2\Pi_g$ and the excited $A^2\Pi_u$ curves are quite similar. The equilibrium bond distance for the ground state is 2.58 a_0 and the dissociation energy 3.93 eV, compared to 2.55 a_0 and 4.21 eV from [7]. The latter results are in almost perfect agreement with the experimental values 2.53 a_0 and 4.16 eV [11], respectively. For the $A^2\Pi_u$ state there is a minimum for longer bond distances with a valence-like wavefunction. For this outer minimum we obtain a bond distance of 3.49 a_0 and a binding energy of 0.75 eV, compared to 3.43 a_0 and 0.81 eV from [7]. For shorter bond distances, the $A^2\Pi_u$ state passes through a curve crossing and inside the crossing point the π_u orbital becomes very diffuse in agreement with what is reported in [7]. However, the shape of the curve and the energetic position of the curve crossing differs markedly between the calculations. In [7] the curve crossing occurs at about 3 eV above the asymptote but in our calculations it is found only 1 eV above the asymptote.

The next stage in the calculations on the $A^2\Pi_u$ state was to improve the diffuse part of the wavefunction further. This was done by adding first one additional, even tempered, p-function and then two additional such functions. The resulting curves for the $A^2\Pi_u$ state was shown in Fig. 2. We note that the improvement of the diffuse part of the wavefunction has a dramatic effect on the energetic position of the curve. In the final calculation, including 3 diffuse p-functions, it turns out that the $A^2\Pi_u$ curve nearly coincides with the curve obtained in the same basis for the neutral $X^3\Sigma_g^-$ state, and what has happened is now clear. The three diffuse p-functions are simply describing a free electron. The Rydberg part of the $A^2\Pi_u$ curve is an artefact of the calculations in [6, 7]. The curve crossing is in reality a curve crossing between the $A^2\Pi_u$ curve of O_2^- and the ground state curve of O_2. Inside the crossing point one π_u electron will auto-detach. It can further be noted that if a GTO-exponent is used giving the same $\langle r \rangle$ as the most diffuse STO p-function in [7], then our computed curve will almost coincide with the curve obtained in [7] (see Fig. 2).

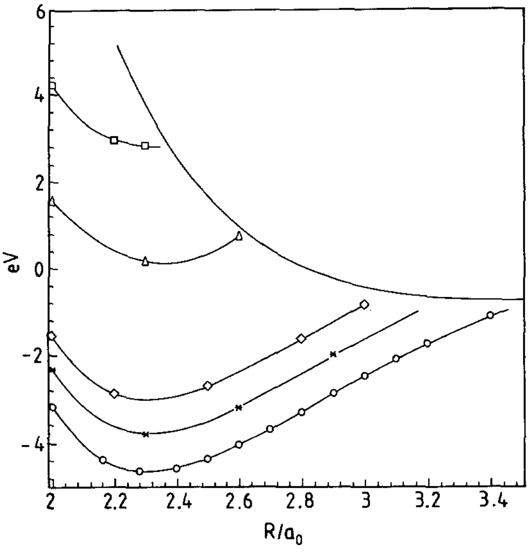

Fig. 2. The $^2\Pi_u$ potential curve obtained using a successively increased number of diffuse p-functions: △, 1 diffuse p-function; ◇, 2 functions, and ☆, 3 functions. Also shown is the ground state curve of neutral O_2 (○) and an extrapolation of the outer region of the $A^2\Pi_u$ curve towards shorter bond distances. The curve marked (□) nearly coincides with the one reported in [7] and is obtained using a diffuse p-exponent of 0.11

In these types of calculations it may sometimes be difficult to differentiate between a situation where an electron wants to auto-detach and when it wants to occupy a diffuse Rydberg state. To identify the former situation, it can therefore be useful to know how the total energy in that case will depend on the value of the exponent of a diffuse Gaussian basis function. If we make the simplification that the diffuse orbital is described by a single Gaussian function, $\propto r^n e^{-\beta r^2} Y_{lm}$, the kinetic energy is given by

$$\langle T \rangle = \langle -\tfrac{1}{2}\nabla^2 \rangle = \beta \left[(n + \tfrac{3}{2}) - 2\,\frac{n(n+1) - l(l+1)}{2n+1} \right].$$

The potential energy of the particle is dependent on the properties of the core. For a core which has a charge q, or a dipole moment μ or a polarizability α the potential $\langle V \rangle$ will be proportional to $q\beta^{1/2}$, $\mu\beta$ or $\alpha\beta^{3/2}$, respectively. For a charged core there will always exist Rydberg states, as can easily be seen by a minimization of $\langle T + V \rangle$ with respect to β. However, for a dipole field or an induced dipole field the situation is more complicated. In the former case the derivative of the total energy will not give a minimum, indicating that the potential may not be strong enough to bind the particle. In the case of an induced dipole field one must also take into account the increase in energy upon polarizing the core, the net effect being that also this field may be too weak to hold Rydberg levels.

In the case of an auto-detaching state, the minimum in energy is obtained by utilizing the most diffuse part of the basis set, subject to orthogonalization of the diffuse orbital with respect to the core, since this minimizes the kinetic energy of the detaching particle. As the basis set is enriched with diffuse functions the energy gain should be largely determined by the decrease in kinetic energy, and it will thus follow a linear relationship with the smallest orbital exponent. This behaviour is contrary to what is found in the case of Rydberg and other bound states, where only functions with exponents in a small range (on a relative scale) lower the energy significantly.

For the present case of the $A^2\Pi_u$ state of O_2^- the relevant choice of parameters in the expression for the kinetic energy are $n = l = 1$, giving $\langle T \rangle = \frac{5}{2}\beta$. In the calculations (of which some are shown in Fig. 2), five different β values were used for the most diffuse p-function. A least square linear fit of the energy as a function of these values of β (for a fixed internuclear distance of $R = 2.30\ a_0$), gives a fit with a regression coefficient of 0.998. The proportionality factor between the total energy and the exponent β is 2.41, in close agreement with the value 2.50 as given from the formula for the kinetic energy. Furthermore, the constant term is only 0.04 eV above the ground state energy of O_2 calculated in the same basis set. There is thus no doubt in the present case that the diffuse function is trying to describe a free electron and not a diffuse Rydberg state.

4. Conclusions

The potential curve of the excited $A^2\Pi_u$ state of O_2^- has been studied in detail. For long bond distances ($R > 3.3\ a_0$) the electronic wavefunction is found to be valence-like in agreement with previous studies. For shorter bond distances the present study shows that an electron will auto-detach. This is in contrast to a previous study where the wavefunction was found to have Rydberg character in the inner region of this potential curve. The Rydberg character is only obtained if the basis set lacks diffuse enough p-functions. Making the outermost p-function more and more diffuse eventually leads to a description of a free electron. It is demonstrated by calculations that the total energy depends linearly on the exponent of the most diffuse Gaussian p-function with a proportionality factor which is close to the analytically derived value $\frac{5}{2}$.

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