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Applying Monte Carlo configuration interaction to transition metal dimers: Exploring the balance between static and dynamic correlation

J.P. Coe, P. Murphy, M.J. Paterson [*]

Institute of Chemical Sciences, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, United Kingdom

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ABSTRACT

We calculate potential curves for transition metal dimers using Monte Carlo configuration interaction (MCCI). These results, and their associated spectroscopic values, are compared with experimental and computational studies. The multireference nature of the MCCI wavefunction is quantified and we estimate the important orbitals. We initially consider the ground state of the chromium dimer. Next we calculate potential curves for Sc_2 where we contrast the lowest triplet and quintet states. We look at the molybdenum dimer where we compare non-relativistic results with the partial inclusion of relativistic effects via effective core potentials, and report results for scandium nickel.

1. Introduction

Transition metals can be very challenging for computational chemistry methods due to the existence of many important configurations at numerous geometries. This means that methods that can cope with multireference systems, and their associated computational costs, are often necessary. In addition, accurate modelling of heavy transition metals may also require relativistic effects to be incorporated.

Although full configuration interaction (FCI) will produce the most accurate wavefunction in a given basis, the number of configurations that would need to be considered for transition metal dimers makes this method currently computationally intractable. A powerful approach to attempt to overcome this problem is complete active space SCF (CASSCF) [1] which efficiently calculates a wavefunction comprising all configurations formed from substitutions within a restricted set of orbitals by optimising coefficients and orbitals. This method is thought to model much of the static correlation which is associated with a few important configurations in the FCI wavefunction. The remaining difference is then termed dynamic correlation and this can be accounted for by multireference CI (MRCI) or perturbative corrections such as CASPT2 [2].

Monte Carlo configuration interaction (MCCI) [3] aims to find a compact, yet sufficiently accurate, description of the FCI wavefunction by iteratively building up a wavefunction through the random addition of configurations without requiring knowledge of the important orbitals before a calculation. Recent successful applications of MCCI include excitation energies [4,5] and properties [6]. MCCI with complex wavefunctions has been used in the modelling of a tunnel junction consisting of gold atoms [7]. MCCI has been demonstrated to produce potential curves of ground states [8] that generally compared favourably with the FCI results using just a small fraction of the FCI space for small molecules. Excited potential curves, including avoided crossings and conical intersections, for small systems were seen to be similar to FCI results, but used a compact wavefunction when calculated with SA-MCCI in Ref. [5]. It is therefore interesting to investigate the potential curves of transition metal dimers with MCCI as a stern test of the method when the division between static and dynamic correlation becomes blurred and for the possibility of supporting the choice of active spaces as appropriate in other computational work. We aim to demonstrate that MCCI can model a selection of transition metal dimers without prior knowledge of the important orbitals or resorting to perturbative corrections. The compact nature of the MCCI wavefunction then allows us to quantify its multireference character using all of the included configurations. We also estimate the important orbitals for a representative sample of the considered geometries. We compare the MCCI calculations with other computational work and experimental results for the chromium dimer with a cc-pVDZ and cc-pVTZ basis then Sc_2 with the same bases. We then look at the potential curve for the molybdenum dimer using a minimal basis (STO-3G) followed by LANL2DZ and Stuttgart RSC to approximate relativistic corrections. Finally we consider ScNi, with the STO-3G basis, as an example of a heteronuclear diatomic.

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[*] Corresponding author. Fax: +44 (0)131 451 3180.
E-mail address: m.j.paterson@hw.ac.uk (M.J. Paterson).

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2. Method

We use version four of the MCCI program [3,9]. We always use the Hartree–Fock (HF) molecular orbitals (MOs) for consistency and the necessary integrals are calculated using Molpro [10]. The MOs are employed in the following calculations which begin from the configuration state function (CSF) formed from the occupied HF MOs. The current set of CSFs is augmented with new CSFs created using symmetry-preserving random single and double substitutions of MOs. The Hamiltonian matrix is created and diagonalized in this set of CSFs and any new configurations with an absolute coefficient less than c_{min} in the resulting wavefunction are removed. The process is repeated and every ten iterations all CSFs in the wavefunction are considered for removal (full pruning). The program is run until the convergence criterion for the energy, as detailed in Ref. [4], is satisfied. We consider the average energy for the last three full pruning steps. Results were calculated using an initial 10^{-3} Hartree convergence check and then a 5×10^{-4} Hartree convergence check unless otherwise stated. We implement calculations initially at $c_{\text{min}} = 5 \times 10^{-4}$ then lower this value until a sufficiently smooth potential curve is achieved.

We calculate vibrational energy levels of the potential curve for the most abundant isotopes with the program LEVEL 8.0 [11]. The transition metal potential curves can display a secondary well and will not adhere to the form of the Morse potential [12]. We therefore use the lowest energy level to approximate the harmonic vibrational frequency (ω_e). Due to MCCI not being size consistent, we calculate dissociation energies as the difference between the energy at equilibrium, with the ground state vibrational energy included, and the longest bond length considered.

We quantify the multireference character associated with the MCCI wavefunction for a given basis and set of MOs using

$$MR = \sum_i |c_i|^2 - |c_i|^4. \tag{1}$$

Here the c_i are normalised so that $\sum_i |c_i|^2 = 1$. The expression is approximate when using CSFs due to their non-orthogonality. A value of zero will result from a single configuration in the wavefunction while unity will be approached as the coefficients become equal in magnitude and more numerous. We also measure the importance of MOs in the MCCI wavefunction by considering the percentage of configurations they occur in where each occurrence is weighted by $|c_i|^2$.

3. Results

3.1. Chromium dimer

The availability of a potential curve based on experimental results and the difficulty of the system to model makes Cr_2 useful for testing methods. The fitted curve [13] did not display the barrier necessary for a double well, as was seen in an early computational study [14], but due to a lack of vibrational data the experimental potential is not known as accurately in this region. The bond length has been found experimentally as $R_e = 1.6788$ Å [15] and the dissociation energy has been measured as 1.53 ± 0.06 eV in Ref. [16] while Ref. [13] finds $\omega_e = 480.6\ \text{cm}^{-1}$ and $\omega_e \chi_e = 14.1\ \text{cm}^{-1}$. For theoretical results, it appears that a good treatment of both dynamic and static correlation is necessary to give a sufficiently accurate potential energy curve: Ref. [17] depicts how the potential curve from CASSCF (12,12) is seen to be repulsive for small bond lengths with a weakly attractive minimum around 3 Å, but CASPT2 can produce a realistic potential. CASPT2 and similar approaches have also been used in, e.g., Refs. [18–21] with generally high accuracy. Ref. [18] found the curve was dependent on the choice of zeroth-order Hamiltonian, but is particularly close to experimental results when using CASPT2 IPEA 0.45 with the equilibrium bond lengths found to be around 1.68 Å and $D_0 = 1.50$ eV with a vibrational interval of 542 cm^{-1}. However CASPT2 results in [21] were not so accurate and found a longer bond length of 2.43 Å and a lower dissociation energy of 1.0 eV. Multireference coupled cluster [22] gave complete basis set estimates of $R_e = 1.685$ Å, $D_0 = 1.327$ eV and $\omega_e = 459\ \text{cm}^{-1}$. A double well was observed when using a TZP basis but not with a QZP basis.

When using MCCI to model an A_g singlet in Cr_2, we freeze 18 orbitals and, for consistency in the HF curve, we require that the HF wavefunctions have the same occupation of orbitals from each symmetry class. The HF energies at 1.4 Å were -2085.9767 Hartree for cc-pVDZ and -2085.9945 Hartree for cc-pVTZ. With the cc-pVDZ basis and $c_{\text{min}} = 5 \times 10^{-4}$, the energy at bond lengths of 6 and 3.5 Å appeared as though they may be anomalously high when using a convergence check of 10^{-3} Hartree. We attempted to improve the energies at these points by using the result of the next shorter bond length as a starting point. The energy at $R = 6$ Å was improved substantially using this approach but the $R = 3.5$ Å calculation did not give a lower energy. A small barrier remains in this region when using a tighter convergence check suggesting that it may be a feature of the MCCI calculation at this c_{min}. We then considered a lower cut-off of $c_{\text{min}} = 2 \times 10^{-4}$. Here one point was not calculated due to time constraints. The results were closer to the experimental curve, but a secondary well was now seen.

For the cc-pVTZ basis we initially used $c_{\text{min}} = 5 \times 10^{-4}$ however this resulted in a curve which was not smooth. Hence the points were recalculated using $c_{\text{min}} = 2 \times 10^{-4}$ with the larger c_{min} result used as the starting point. This gave a smooth curve except for two points which appeared too high in energy compared with the rest of the curve: 2.75 and 6 Å. They were much improved when the calculation was restarted using the configurations of the next shorter bond length as the starting point. The results are displayed in Figure 1 with the fitted experimental results from Ref. [13] also plotted for comparison. The results agree with the experimental curve for the inner wall and equilibrium geometry, but at intermediate geometries the cc-pVDZ curve increases too rapidly and this effect is more pronounced when using the cc-pVTZ basis although this increase is moderated when using cc-pVDZ with the lower c_{min}. We note that CASPT2 results can be very close to the experimental curve but this requires tailoring of both the active space and zeroth-order Hamiltonian.

On lowering the cut-off in cc-pVDZ the vibrational frequency changed from 734 to 490 cm^{-1} giving a better agreement with experiment, but the dissociation energy reduced from 1.41 to

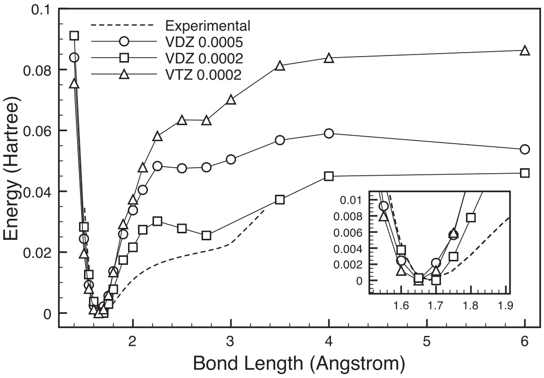

Figure 1. Energy (Hartree) shifted so that all minima are at zero against bond length (Å) for the chromium dimer for the experimental results compared with MCCI ($c_{\text{min}} = 5 \times 10^{-4}$ or $c_{\text{min}} = 2 \times 10^{-4}$) using cc-pVDZ and MCCI ($c_{\text{min}} = 2 \times 10^{-4}$) using cc-pVTZ both with 18 frozen orbitals. Inset: an enlarged view of the minima.