AN ACCURATE AB INITIO CALCULATION OF THE He₂ POTENTIAL CURVE

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The ability of ab initio quantum-chemical methods to produce very accurate potential energy curves for van der Waals molecules is demonstrated through the calculation of the helium dimer interaction energy for a variety of internuclear distances around the van der Waals minimum (R = 5.6 bohr). At the minimum we obtain in actual calculation \(-10.86 \text{ K}\), whereas the estimated limit for the interaction energy is \(-10.98 \pm 0.03 \text{ K}\) in close agreement with a recent empirical result of \(-10.948 \text{ K}\) (HFD-B potential of Aziz, McCourt and Wong).

1. Introduction

In spite of the smallness of the He₂ system, ab initio calculations of the He₂ potential have up to now not been able to match the accuracy of semi-empirically determined interaction potentials. This is due to three problems in the ab initio approach: the size of the requisite basis set, the inadequacy of standard methodology and the basis set superposition error (BSSE). Admittedly, some ab initio He₂ potentials which agreed well (within 0.1-0.3 K) with available experimental data have recently been published. Notably, at 5.6 bohr the interaction energy \(E_{\text{int}}\) was calculated as \(-10.76 \text{ [1]}, -10.55 \text{ [2]}\) and \(-10.58 \text{ K [3]}\). However, the agreement was to some degree fortuitous. For example, the Liu and McLean [1] result is lowered by almost 1 K upon saturation of the basis set [4]. Likewise, incomplete description of correlation effects, as in the MP4 method and in the SDCI CEPA method, causes \(E_{\text{int}}\) to be underestimated by 1-2 K [5,6]. On the other hand, failure to correct supermolecular calculations for BSSE may cause \(E_{\text{int}}\) to be overestimated by as much as 40 K [6]. Thus virtually any \(E_{\text{int}}\) in the range –8 through –50 K can be generated, depending on the details of the calculations, and it is not surprising that some calculations did in fact produce “good agreement” with experiment. In the light of these findings a calculated potential can only be said to be accurate to the extent that saturation of the basis set and of the configuration set have been demonstrated in actual calculation, while BSSE is effectively eliminated. Few studies, if any (cf. ref. [7]) that meet all those three requirements have yet appeared in the literature. We have therefore undertaken such a study on the He₂ system. In this Letter we present preliminary results which show that an accuracy in the potential of better than 0.1 K (at 5.6 bohr) can be achieved in calculations which, by current standards, are of a practicable size.

The He dimer was chosen since its size permits extensive numerical experimentation [5,6,8-10]. Moreover, a number of recent experiments [11-13] have enabled the determination of a new empirical potential energy curve (HFD-B) [14] which shows a minimum of \(-10.95 \text{ K}\) at 5.6 bohr, substantially lower than previous estimates [15]. This potential may be instrumental [14] in correlating experimental data like second virial coefficients, needed for measurements of low temperatures, as well as viscosity and thermal conductivity data, required to assign error limits to a determination of the universal gas constant \(R\) from measurements of the sound velocity in helium. Support from accurate ab initio calculations could promote the acceptance of the HFD-B potential as a new standard.
2. Basis set superposition error

The first and most serious problem in accurate ab initio calculations of van der Waals interaction potentials is the BSSE [16] which arises from the difference in basis set between monomer and dimer. In our calculation we have employed the counterpoise procedure (CP) [17] to eliminate BSSE. The reliability of this procedure used to be viewed with scepticism. Recently, however, careful numerical proof of the validity of the counterpoise recipe as well as formal arguments in favour of it have been supplied both at the Hartree–Fock [8] and CI [6,18] levels of theory. As part of the present study, further experiments have been carried out on He* [19] in which we compared the (repulsive) intra-correlated CEPA interaction energy [9], with the (repulsive) first-order interaction energy $E'(I)$ for correlated monomers [20]. The former was CP-corrected for BSSE as in the work by Meyer et al. [9], whereas the latter is free of BSSE. Apart from some relaxation terms not present in $E'(I)$, the two quantities should resemble each other fairly closely. In practice we found that in a sequence of basis sets with widely different BSSE and differences in $E''(I)$ of up to 0.5 K, the changes in the energies were equal to within 0.001 K at 5.6 bohr, i.e. to the precision of the calculations. This means that the counterpoise procedure has succeeded in fully removing the monomer-energy-related artefacts from the CEPA calculations, confirming that it yields the CEPA interaction energy for a given (dimer) AO basis set (cf. refs. [6,8]). The counterpoise recipe requires the parameter spaces in the monomer and dimer calculations to be equal [17], i.e. in a CI calculation the (formal) excitation possibilities should match. It is not obvious that this can always be achieved in practice. Within the above constraint, the basis set optimization as well as the choice of the (CI) method may concentrate on the optimal description of the interaction energy components rather than on reducing the BSSE.

3. Configuration interaction approach

Our calculations employ the multi-reference CI model [21], allowing all single and double excitations with respect to a user specific multi-configura-

4. Basis sets

Two basis sets were used. The one labeled small is a (15s, 3p, 2d) + (6s, 3p, 2d) (50 AOs) basis, where the most diffuse p and d AOs are specially optimized for the dispersion interaction. The large basis was developed from the C2D5 set of ref. [6]. To this set we added a set of correlating f functions and a number of bond functions for a better description of the dispersion energy [10,26]. The resulting 159-AO basis consists of a [7s, 4p, 4d, 2f, 1g, 1h] set on each
helium augmented by one set of d bond functions and two sets of s and p bond functions. In the MR CI calculations, its size was reduced to 131 AOs by removing all higher than 6 components in order to comply with the restrictions imposed by our computer system. This can be done at little loss of accuracy (<0.01 K at 5.6 bohr). Indeed the final 131-AO set yields slightly better dispersion energies than the 178-AO "LARGE" set of ref. [26].

In order to monitor the quality of the basis sets separate perturbation theory calculations were done to obtain the repulsive correlated first-order energy \( E^{(1)} \) [20] and the second-order polarization dispersion energy \( E_{\text{disp}} \) [26]. The required monomer wavefunctions were expressed in the full dimer basis set \( E^{(1)} \) and \( E_{\text{disp}} \) are the main contributors to \( E_{\text{int}} \); they are free from BSSE and their basis set limits are easier to attain than that of the MR CI calculations. Table 1 contains some results for the van der Waals minimum (\( R=5.6 \) bohr) and the repulsive wall (\( R=4.0 \) bohr). \( E^{(1)} \) is almost converged in the large basis, whereas \( E_{\text{disp}} \) is still above the converged result. Our calculated curve must therefore lie above the real one. Since table 1 shows that the change in \( E^{(1)} + E_{\text{disp}} \) between basis sets is neatly reflected in the MR CI interaction energy, we may, using the currently best results for \( E^{(1)} \) and \( E_{\text{disp}} \), tentatively extrapolate to find limiting values for \( E_{\text{int}} \) of \(-10.98 \pm 0.03 \) K at \( R=5.6 \) bohr and \( 294 \pm 2 \) K at \( R=4.0 \) bohr.

### Table 1

<table>
<thead>
<tr>
<th>Basis set</th>
<th>Small</th>
<th>Large</th>
<th>Current best</th>
<th>Previous best</th>
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<tr>
<td>( R=5.6 ) bohr (2.96 Å)</td>
<td>( E^{(1)} )</td>
<td>10.72</td>
<td>10.63 b)</td>
<td>10.63</td>
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<td>( E_{\text{disp}} )</td>
<td>-15.40</td>
<td>-17.02</td>
<td>-17.08</td>
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<tr>
<td></td>
<td>( E_{\text{int}} ) (MR CI)</td>
<td>-9.08</td>
<td>-10.86</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BSSE</td>
<td>2.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( R=4.0 ) bohr (2.12 Å)</td>
<td>( E^{(1)} )</td>
<td>494.7</td>
<td>492.7 b)</td>
<td>492.6</td>
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<tr>
<td></td>
<td>( E_{\text{disp}} )</td>
<td>-125.2</td>
<td>-153.0</td>
<td>-154.4</td>
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<tr>
<td></td>
<td>( E_{\text{int}} ) (MR CI)</td>
<td>323.1</td>
<td>296.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BSSE</td>
<td>5.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Estimated using CEPA(1) results in this basis. b) Taken from work in progress. c) Ref. [20]. d) Ref. [26]. e) Ref. [27].

### 5. Results and discussion

Table 2 presents a comparison of our large-basis interaction energies with the HFD-B curve, for the full range 2.0–8.0 bohr. At long range, where the experimental curve is based on accurately known \( C_6 \), \( C_8 \), and \( C_{10} \) coefficients, the agreement is excellent. At 6.0 bohr our result is slightly below the HFD-B curve. Between 4.0 and 5.6 bohr our curve is above it, but, as noted above, the use of a better basis and a slightly larger set of reference configurations should close the gap. At short \( R \) our curve is in good agreement with the ab initio Monte Carlo results of Ceperley and Partridge [28] (\( R=2.0 \) bohr, \( E_{\text{int}}=35800 \pm 150 \) K; \( R=3.0 \) bohr, \( E_{\text{int}}=3800 \pm 100 \) K); this agreement is actually better than that of Aziz et al., who in their fitting procedure used the \( R=1.0 \) result from Ceperley and Partridge. These data suggest that the HFD-B potential, while essentially correct, is a little too repulsive for \( R<4.0 \) and for \( R \approx 6 \) bohr.

Since we monitored the convergence of both major components of the interaction energy and since the BSSE is completely accounted for, no fortuitous cancellation of errors can occur in our results. We conclude that state-of-the-art ab initio theory is capable of attaining high accuracy in calculations of intermolecular potentials.

The accuracy of about 1% obtained here for the very weakly bound He* system requires large basis sets in order to saturate the dispersion energy, which is more than twice the interaction energy itself. In more typical van der Waals complexes the dispersion energy is less dominating and moreover the ac-
Table 2
He-He interaction potential in K

<table>
<thead>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(this work)</td>
<td>(this work)</td>
</tr>
<tr>
<td>2.0</td>
<td>36329.1</td>
<td>3696.1</td>
<td>36383.3</td>
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<td>-4.61</td>
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<td>-2.06</td>
<td>-1.99</td>
<td>-2.06</td>
</tr>
<tr>
<td>8.0</td>
<td>-2.07</td>
<td>-2.06</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Accuracy requirements are less stringent, so relatively smaller configuration sets and basis sets may be used. We are therefore confident that counterpoise-corrected MR CI calculations are a viable means to obtain good potential energy surfaces for van der Waals complexes.

Acknowledgement

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References


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