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Letters to the Editor

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Communications

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Accurate calculation of the attractive interaction of two ground state helium atoms

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No theoretical study of the van der Waals interaction of two ground state helium atoms has yet been successful in predicting the depth ϵ_m of the attractive well to within a desirable accuracy of $\sim 0.1\,^\circ\mathrm{K}$. Recent calculations including only interatomic correlation gave $\epsilon_m = 12.02\,^\circ\mathrm{K}$.[1-3] Bertoncini and Wahl calculated a correction of $1.23\,^\circ\mathrm{K}$ due to changes in intra-atomic correlation with nuclear separation and gave $\epsilon_m = 10.79 \pm 0.3\,^\circ\mathrm{K}$,[4] well within the $10.4\,^\circ\mathrm{K}$[5] to $11.2\,^\circ\mathrm{K}$[6] range estimated from experimental data. However, this correction adversely affects the long range behavior of the curve, and still neglected is the interaction of intra- and interatomic correlation effects.[4] The present configuration interaction (CI) calculation, simultaneously including all of these effects, is designed to converge on the exact clamped nuclei result within an accuracy of $\sim 0.1\,^\circ\mathrm{K} = 3\times10^{-7}$ a.u. for the interaction energy $\Delta E(R) = E(R) - E(\infty)$. This extraordinary demand on accuracy means that correlation energy changes with R must be correct into the sixth significant figure of the correlation energy, in the face of basis set deficiencies which give rise to absolute errors in the correlation energy in the second significant figure.

The most difficult computational task turned out to be avoiding a "basis set superposition error" the existence of which can be understood from the following example. Compare two complete CI He atom calculations (1) in a basis set of functions defined with the atomic nucleus as origin, and (2) in a basis containing these same functions plus an equivalent set with origin R distant from the atomic nucleus. The energy in the second calculation will be lower than in the first except in the limit of a complete one-center basis. Carried over to the He_2 interaction, the possibility of an artificially deep well can be seen; we have demonstrated the effect in actual calculation. As a consequence of superposition error it is essential to (1) separate those configurations containing intra-atomic correlation effects from those containing interatomic effects by using localized orbitals[1-4] and to (2) determine, for a given basis set, the maximum level of intra-atomic correlation that can be included in a calculation without introduction of unacceptable superposition error, by comparing equivalent atomic CI calculations carried out in one- and two-center basis sets as in the example above.

At each R, three calculations were done to obtain orbitals. (1) A self consistent field (SCF) calculation in the given one-particle basis producing $1\sigma_g$, $1\sigma_u$ orbitals, followed by a localization $\sigma_A = (1/\sqrt{2}) \times (1\sigma_g + 1\sigma_u)$, $\sigma_B = (1/\sqrt{2})(1\sigma_g - 1\sigma_u)$. (2) A CI calculation in the four-particle space $\sigma_A^2\sigma_B^2$, $\{\sigma_A^2, \sigma_B^2\} \otimes \{\text{two electrons into the SCF virtual space}\}$, followed by a transformation of the SCF virtual orbitals to natural orbitals, $NO_{(2)}$. (3) A CI calculation in the space $\sigma_A^2\sigma_B^2$, $\{\sigma_A\sigma_B\} \otimes \{\text{two electrons in the SCF virtual space}\}$, followed by a transformation of the SCF virtual orbitals to $NO_{(3)}$. Orbitals for the CI calculation of $\Delta E(R)$ were σ_A, σ_B, leading occupation members of $NO_{(2)}$, and leading occupation members of $NO_{(3)}$ orthogonalized successively to preceding orbitals until the original one-particle space is spanned. Members chosen from $NO_{(2)}$ are optimum for configurations containing the intra-atomic correlation effects, those from $NO_{(3)}$ for

TABLE I. Interaction energies of two gound state helium atoms (in degrees Kelvin).[a]

R(Å)	$\Delta E(R)$	$\Delta E_{\mathrm{SCF}}(R)$	$\Delta E_{\mathrm{mol}}(R)$	$\Delta E_{\mathrm{at+mol}}(R)$
1.588	3845	4269	3669	3804
2.117	312	428	272	300
2.381	67.9	132	50.7	61.6
2.646	4.10	39.6	−3.57	0.37
2.752	−3.92	24.4	−9.47	−6.93
2.858	−7.69	15.0	−11.7	−10.1
2.963	−9.07	9.21	−12.1	−11.0
3.069	−9.14	5.64	−11.4	−11.0
3.175	−8.58	3.45	−10.2	−10.2
3.704	−4.33	0.28	−4.81	−4.85
4.233	−1.98	0.02	−2.15	−2.21
5.292	−0.49	0.00	−0.53	−0.55
10.583	0.00	0.00	0.00	0.00

[a] $\Delta E(R)$ is from a CI calculation containing all classes of configurations. $\epsilon_m = \Delta E(3.02\ \text{Å}) = 9.23\ ^\circ\text{K}$. $E(\infty) = -5.79503131$ a.u. $\Delta E_{\mathrm{SCF}}(R)$ is the SCF result. $E_{\mathrm{SCF}}(\infty) = -5.72335906$ a.u. $\Delta E_{\mathrm{mol}}(R)$ is from a CI calculation which includes $\sigma_A^2\sigma_B^2$, all single excitations, and $\{\sigma_A\sigma_B\} \otimes \{\text{two electrons into remaining space}\}$. $\Delta E_{\mathrm{at+mol}}(R)$ adjusts $\Delta E_{\mathrm{mol}}(R)$ by the change in ΔE from ΔE_{SCF} on addition of intra-atomic terms to the SCF configuration. Comparison of $\Delta E_{\mathrm{at+mol}}(R)$ with $\Delta E(R)$ shows the lack of additivity of the inter- and intra-atomic correlation affects.

dispersion effects.

In the CI calculations of $\Delta E(R)$, members of different classes of configuration were included to different levels of orbital truncation until convergence was demonstrated. These classes included all types of excitation from the reference configuration, $\sigma_A^2\sigma_B^2$, through quadruples, taking care to restrict the choice of configurations to a level which did not introduce unacceptable superposition error. Parallel calculations were carried out starting from two independent one-particle basis sets to complete the convergence studies. The results of Table I computed with the smaller one-particle basis give a curve with $\epsilon_m = 9.23\ ^\circ\text{K}$ at $R = 3.02$ Å which crosses the energy asymptotic at $r_0 = 2.69$ Å. While refined calculations in the layer basis are not yet complete, our present evidence indicates that the likely change at the minimum in the curve on extrapolation to the exact clamped nuclei nonrelativistic result will be to deepen the well by not more than 0.3 °K. Beyond ~4.0 Å both Table I and the refined results agree with accurate perturbation theory results to within 0.02 °K.[7,8] Our results for inter- and intra-atomic correlation agree with previous theoretical results. The major discrepancy with previous theoretical estimate of $\epsilon_m = 10.79 \pm 0.3$ °K[4] is due to the coupling of inter- and intra-atomic correlation. Table I shows how this coupling invalidates the additivity of the two types of correlation.

Resolution of the present results with experimental estimates both through calculation of observables, as well as through estimation of Born–Oppenheimer corrections, is in progress.

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