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Dissociation Energies of He$_2^+$($X\,^2\Sigma_u^+$) and He$_2$($A\,^1\Sigma_u^+$)

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The configuration-interaction method is applied to calculate the dissociation energy of He$_2^+$($X\,^2\Sigma_u^+$), yielding a rigorous lower bound of 2.454 eV and a best value of 2.469 ±0.006 eV. These results are used, in combination with available spectroscopic data on vibrational states of the $A\,^1\Sigma_u^+$ state of He$_2$, to unequivocally make an assignment of 2.549 ±0.012 eV for the apparent dissociation energy and to predict a barrier height of 0.080 ±0.018 eV for this state.

Recent high-resolution studies of the He$_2^+$ spectrum have provided precise data for the six lowest and six highly excited vibrational levels of the $A\,^1\Sigma_u^+$ state of He$_2$.[1] From these data it is possible to restrict the dissociation energy of the A state to a set of discrete values separated by ~0.15 eV, depending on the assignment of vibrational quantum numbers to the excited levels.[2-4] Ginter and Brown[4] gave apparent dissociation energies E_e, the difference between the top of the barrier in the He$_2$ potential curve and the potential minimum, for six possible vibrational assignments. Using theoretical values for the equilibrium dissociation energy D_e for He$_2^+$ ($X^2\Sigma_u^+$), which is known to differ from that of He$_2$($A\,^1\Sigma_u^+$) by ~6×10^{-4} eV,[5] and an assumed barrier height of ~0.05–0.07 eV, they eliminated three of the six possible assignments. The remaining values of E_e are 2.402±0.012, 2.549 ±0.012, and 2.687±0.019 eV. The first value is obtained from a vibrational assignment proposed by Smith and Chow[2] and is supported by several theoretical values.[6] The second value comes from a vibrational assignment proposed by Sando[3] and is supported by still another theoretical value.[7] This report presents results of an *ab initio* study of He$_2^+$, which yields for $D_e(X^2\Sigma_u^+)$ a rigorous lower bound of 2.454 eV and a probable value of 2.469±0.006 eV, establishing unambiguously that the vibrational assignment proposed by Sando is correct.

The calculations use the usual nonrelativistic Hamiltonian, Born-Oppenheimer approximation, and the conventional configuration-interaction (CI) method. Each configuration is a symmetry-adapted linear combination of Slater determinants of orthogonal molecular orbitals. The molecular orbitals are expanded in terms of Slater-type functions (STF) on the He nuclei.

Table I presents series of calculations, at an internuclear separation of 2.0625 a.u., which demonstrate the accuracy of the current results. Series I and II show convergence of the calculations with respect to inclusion of configurations, using a common STF basis of four s, three p, two d, and one f functions on each nucleus, taken from Weiss.[8] The occupied Hartree-Fock (HF) orbitals for the dominant configuration $1\sigma_g^2\,1\sigma_u$ were determined within this STF basis, together with a set of virtual orbitals which with the HF orbitals span the original STF basis. Two CI calculations were then carried out: (a) The dominant configuration $1\sigma_g^2\,1\sigma_u$ was mixed with all configurations related to it by single or double excitations into the set of virtual orbitals. The configurations $1\sigma_u(n\lambda\, m\lambda,\ ^3\Sigma_g^+)$ were considered as triple excitations, since they do not interact with the dominant configuration. (b) $1\sigma_g^2\,1\sigma_u$ was

TABLE I. $He_2^+(X\,^2\Sigma_u^+)$: CI and basis-set convergence study. $R = 2.0625$ a.u.

No. of NO's[a]				E_I[b] (a.u.)	E_{II}[c] (a.u.)	$E_I - E_{II}$ (a.u.)	E_{IV}[b] (a.u.)	$E_I - E_{IV}$ (a.u.)
σ	π	δ	ϕ					
1				-4.92237	-4.92237	0.00000	-4.92238	0.00001
3				-4.97194	-4.97215	0.00021	-4.97208	0.00014
6				-4.97436	-4.97462	0.00026	-4.97473	0.00037
10				-4.97481	-4.97508	0.00027	-4.97511	0.00030
15							-4.97523	
A[d]	1			-4.98877	-4.98919	0.00042	-4.98919	0.00042
A	3			-4.99102	-4.99150	0.00048	-4.99143	0.00041
A	6			-4.99149	-4.99197	0.00048	-4.99193	0.00044
A	10						-4.99209	
A	A	1		-4.99222	-4.99272	0.00050	-4.99281	0.00059
A	A	3		-4.99250	-4.99300	0.00050	-4.99310	0.00060
A	A	6					-4.99321	
A	A	A	1	-4.99261	-4.99311	0.00050	-4.99332	0.00071
A	A	A	A	-4.99261	-4.99311	0.00050	-4.99338	0.00077

[a] Same number of gerade and ungerade orbitals are included from each symmetry. The numbers given here apply to both.

[b] Energies from all singles and doubles calculations.

[c] Energies from complete CI calculations.

[d] *A* means all natural orbitals of a symmetry.

mixed with all configurations which can be constructed from the orbital basis (complete CI). The spinless natural orbitals were determined for both these CI wave functions, denoted NO_a and NO_b, respectively.

In Table I, series I gives the results of a further sequence of CI calculations including the dominant configuration with all singles and doubles constructed from NO_a, at various levels of truncation to decreasing occupation numbers. Series II shows a parallel sequence in which at each level of truncation a complete CI calculation was done, with configuration constructed from NO_b. Each series shows the convergence of the calculations with respect to the size of the orbital basis. Comparison of the series shows the effect of triple excitations. The total effect of triples is to lower the energy by 0.0005 a.u., a gratifyingly small amount. More importantly, this lowering is achieved at a level of severe orbital truncation. A third series of calculations repeated series II using orbital set NO_a, yielding results duplicating series II to six significant figures. Thus, beginning with NO_a, even though single and double excitations into the full orbital basis are necessary, higher excitations can be considerably truncated. Whether this result is upheld for more complicated systems is of considerable importance, since complete CI calculations are in general unmanageable.

Series I and IV show convergence of the calculations with respect to the starting STF basis. Series IV repeats series I starting from a STF basis of five *s*, four *p*, three *d*, two *f*, and one *g* functions.[8] The larger STF basis lowers the He_2^+ energy by 0.0007 a.u. and the $He + He^+$ energy by 0.0005 a.u., resulting in a change of only 0.0002 a.u. (~0.0054 eV) in the computed dissociation energy. The HF energy is -4.92269 a.u. for the small STF basis, and is lowered by 0.00001 a.u. when the large basis is used.

Three final calculations, in Table II, show the potential curve around its minimum. Each calculation uses the larger STF basis (series IV above), including all single and double excitations, and triples up to the limit of the sixth σ_g and σ_u and the third π_u and π_g natural orbitals. The natural orbitals were taken from a calcula-

TABLE II. Total energy of He_2^+.

R (a.u.)	E_{HF}(a.u.)	E_{CI}(a.u.)	E_{exact}(a.u.)
2.0	−4.923 09	−4.993 69	...
2.044[a]	...	−4.993 89[a]	−4.994 39 ± 0.0002[b]
2.0625	−4.922 70	−4.993 85	...
2.125	−4.921 53	−4.993 21	...
∞	−4.861 63	−4.903 16	−4.903 72[c]

[a] Interpolated values for the energy minimum.

[b] Estimated value for the exact energy.

[c] See C. L. Pekeris, Phys. Rev. 112, 1649 (1958), and 115, 1216 (1959).

tion including all singles and doubles.

The difference between the computed minimum for He_2^+ and the exact nonrelativistic energy for $He + He^+$ gives a lower bound of 2.454 eV for the dissociation energy. This rules out the $E_e(A\,^1\Sigma_u^+)$ value of 2.402 ± 0.012 eV, since it appears well established that the barrier height is ~0.05 eV.[1,9] Results in Table I and experience with other molecules, such as H_2 and H_3, lead this writer to believe that the correlation error for the computed energy minimum lies between 0.003 and 0.0007 a.u. Since the correlation error in He + He^+ is 0.0005 a.u., this leads to a best value of 2.469 ± 0.006 eV for the dissociation energy of ground-state He_2^+. This is in good agreement with $E_e(A\,^1\Sigma_u^+) = 2.549 \pm 0.012$ eV obtained from Sando's vibrational assignment, and supports a barrier height of 0.080 ± 0.018 eV.

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Energy Transfer in Electron-Exchange Reactions at Low Kinetic Energies*

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The energy transferred in single-electron-exchange processes in Ar^{++}-He and Ar^{++}-D_2 collisions has been experimentally determined for relative kinetic energies below 9 eV. The results confirm the "nearest-resonance" hypothesis for these two representative systems.

The internal energy states of product species resulting from single electron transfer in asymmetric atomic or molecular systems are usually assumed to be those states which are consistent with minimum interchange between kinetic and internal energy. That is, for the process

$$A^+ + B \to B^+ + A + \Delta E, \tag{1}$$

ΔE, the energy defect, is assumed to be small. This "nearest-resonance" hypothesis has been a