TABLE I. Positron lifetimes and intensity.

Sample	$\tau_1 \times 10^{10}$ (sec)	$\tau_2 \times 10^9$ (sec)	I_2 (%)
Hexane (O_2 saturated)	...	1.0±0.2	38±4
Hexane (air saturated)	5.2±1.0	2.40±0.05	35±2
Hexane (degassed)	...	4.0±0.1	34±2
Fluorohexane (O_2 saturated)	3.6±1.0	1.0±0.2	21±4
Fluorohexane (air saturated)	5.1±1.0	2.43±0.05	22±2
Fluorohexane (degassed)	4.2±1.0	3.0±0.1	20±2
Chlorohexane (O_2 saturated)	4.2±1.0	1.2±0.1	10±4
Chlorohexane (air saturated)	4.4±1.0	2.4±0.1	12±2
Chlorohexane (degassed)	4.4±1.0	2.9±0.1	14±2
Bromohexane (O_2 saturated)	4.4±1.0	1.3±0.2	6±4
Bromohexane (air saturated)	4.8±1.0	2.0±0.1	7±2
Bromohexane (degassed)	4.3±1.0	2.0±0.1	6±2
Iodohexane (O_2 saturated)	4.0±1.0	0.8±0.2	4±4
Iodohexane (air saturated)	5.0±1.0	1.2±0.2	...
Iodohexane (degassed)	3.8±1.0	1.5±0.1	4±2
Cyclohexane (O_2 saturated)	4.7±0.5	1.5±0.1	36±2
Cyclohexane (air saturated)	5.1±1.0	2.5±0.1	32±2
Cyclohexane (degassed)	4.7±0.5	3.1±0.1	35±2
Benzene (O_2 saturated)	4.8±1.0	1.3±0.2	...
Benzene (air saturated)	5.1±1.0	2.5±0.2	34±2
Benzene (degassed)	4.9±1.0	3.1±0.1	34±2

measurements on a number of halogen compounds and with the values that we report in Table I. Further, Brandt and Spirn[9] have analyzed glycerol and have taken three components off the delayed coincidence spectrum. Their better time resolution permits this analysis and their τ_B should be closely equal to the τ_1 of this paper. The value of τ_B for glycerol is constant over a temperature range $-185°$ to $+350°C$ and would be $\sim5\times10^{-10}$ sec, in good agreement with the τ_1's reported in Table I at room temperature.

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Lower Bounds for Some Potential-Energy Curves of H_2 and He_2^{++} *

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MANY methods are known for calculating lower bounds to energy eigenvalues,[1] but most suffer from the disadvantage of requiring integrals involving H_2. A more promising approach is that of Miller,[2] in which the lower bounds E^L, to the l lowest eigenvalues, are obtained as the l lowest roots of the secular determinant

$$\det \mid \delta_{ij}(E_{l+1}^0 - E_i^0)^{-1} - \langle \psi_i^0 \mid (E_{l+1}^0 + E^L + H')^{-1} \mid \psi_j^0 \rangle \mid = 0, \quad (1)$$

where $i, j = 1, 2, \cdots, l$ and E_i^0 and ψ_i^0 are, respectively, the eigenvalues and eigenfunctions of the unperturbed operator $H^0 = H - H'$. It is important to realize that E_i^L is a rigorous lower bound to E_i only if $E_{l+1}^0 > E_i^L$. This condition limits the applicability of the method in the case of the excited $^1\Sigma_g^+$ states of H_2. We find that if $H' = 1/r_{12}$, then E_1 lies below E_2^0, but E_2 lies between E_3^0 and E_6^0 (depending on R) and the situation becomes rapidly worse for more highly excited states. However, as the nuclear charge Z increases, the zero-order spacing increases as Z^2, while the interelectronic repulsion increases only as Z. Thus the necessary condition is more easily satisfied by an isoelectronic species of higher Z. Using a 2×2 determinant we were able to apply this method to the two lowest $^1\Sigma_g^+$ states of He_2^{++}, whereas in H_2 a 6×6 determinant would have been required to accomplish this.

The ψ^0's are antisymmetrized products of the one-electron solutions ϕ to the H_2^+ problem. At short internuclear distance R, it is possible to approximate these functions accurately (with an error in the total energy less than 0.0005 a.u.) using a simple James and Coolidge[3] form

$$\phi = Ne^{-a\lambda} \sum_{n,m} C_{nm} \lambda^m \mu^n. \quad (2)$$

In most cases two or three terms were adequate to achieve the required accuracy. As for atoms, a Z expansion is possible and so we can use the H_2^+ wavefunctions for all homonuclear species isoelectronic with H_2. (If all distances are expressed in units of $1/Z$ and energy in units of Z^2, the zero-order equation becomes independent of Z.)[4] These one-electron functions are simple to calculate and because of the integral powers of λ, μ they are easy to integrate, so they should prove to be a useful starting point in molecular calculations.[5] Beyond $R = 4$ a.u. (or 2 a.u. in the He_2^{++} case) the Guillemin–Zener forms were used, as they have the correct asymptotic behavior.[6] The integrals were performed numerically, using a Gaussian quadrature in five dimensions.

TABLE I. Lower bounds from 2×2 determinant.

Spectroscopic state and molecule	R (a.u.)	0.6	1.0	1.2	1.4	1.6	2.0	3.0	4.0	∞		
H_2 X $^1\Sigma_g^+$	$-E_{upper}$[a]	0.7696	1.1245	1.1649	1.1745	1.1686	1.1381	1.0573	1.0164	1.000	···	···
	$-E_{lower}$	0.834	1.175	1.211	1.214	1.203	1.167	1.072	1.026	1.000	···	···

	R (a.u.)	0.8	1.2	1.3	1.4	1.8	2.0	2.2	2.5	3.0	4.0	∞
He_2^{++} X $^1\Sigma_g^+$	$-E_{upper}$[b]	3.356	3.672	3.680	3.678	3.634	3.623	3.621	3.635	3.676	3.751	4.000
	$-E_{lower}$	3.420	3.722	3.725	3.717	3.675	3.648[d]	3.641[d]	3.648[d]	3.680[d]	3.754[d]	4.000

	R (a.u.)	2.0	2.5	3.0	3.25	3.5	3.75	4.0	5.0	6.0	∞	
He_2^{++} $^1\Sigma_g^+$ First excited	$-E_{upper}$[c]	···	2.844	···	2.910	2.9128	2.9127	···	2.906	···	2.9037	···
	$-E_{lower}$	2.746[d]	2.956[d]	3.020[d]	3.026[d]	3.029[d]	3.030[d]	3.028[d]	3.022[d]	3.018[d]	3.004	···

[a] W. Kolos and L. Wolniewicz, J. Chem. Phys. **43**, 2429 (1965).

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[c] J. C. Browne, J. Chem. Phys. **42**, 1428 (1965).

[d] These values were calculated using the functions of Ref. 6. All others were calculated from the form of Eq. (2).

In all cases 3 D accuracy was obtained with a six-point quadrature in each dimension.

All of the results in Table I refer to a 2×2 determinant. Miller[7] found (for He) that as the size of the determinant increases, the improvement in E^L is rapid at first but then becomes negligible. (However, an exact result cannot be obtained unless the continuum is included.) For the ground state a 2×2 or 3×3 is generally satisfactory and we have chosen the former for computational convenience in these exploratory calculations. In the case of the H_2 ground state at $R=1.4$ a.u., a 1×1 gives -1.224 a.u., a 2×2 gives -1.214 a.u. and a 3×3 gives -1.212 a.u., while the exact value is -1.174 a.u. Miller[7] has also noted that the lower bounds obtained from this method are better for excited states than for the ground state. In the case of He_2^{++} the reverse is true because we have used only a 2×2 determinant and a 3×3 or 4×4 is needed to give better convergence for the excited state. It is interesting to observe that the 2×2 results for the excited state of He_2^{++} approach -3.004 as $R\to\infty$. This is identical to the fact that only $1s$ character is present in the asymptotic forms of $1\sigma_g^2$ and $1\sigma_u^2$.[8] A further observation from Miller's work[7] on the He isoelectronic series is that the accuracy of this method increases as Z increases. Here we can generalize this result and say that the percent of error in the lower bounds decreases as Z increases and also as R increases.

The results for the He_2^{++} molecule confirm the presence of a maximum in the ground-state curve (see Ref. a, in Table I) and the existence of a shallow potential well in the excited state (see Ref. c, in Table I). We could obtain an upper bound to D_e for the excited state but the accuracy of the lower bound does not warrant it.

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[7] W. H. Miller (private communication).

[8] This result can be proved theoretically by considering the 2×2 secular equation with the asymptotic forms of $1\sigma_u^2$ and $1\sigma_g^2$ (i.e., $1\sigma_g=1s_b+1s_b$ and $1\sigma_u=1s_a-1s_b$).

Unrestricted Hartree–Fock Solutions for Closed-Shell Molecules*

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IT is well known that even in the case of a closed-shell system a Slater determinant formed from molecular orbitals different for electrons with different spins can give a lower energy expectation value than a Slater determinant having the symmetry properties of the exact wavefunction.[1,2] Such determinants with lower energy have been found in MO LCAO calculations where different atomic orbitals are available for the construction of molecular orbitals occupied by electrons