where $k_{D,eq} \equiv - \langle l \mid L \mid l \rangle$ is the so-called "equilibrium dissociation rate coefficient," then it is easily shown that the moments $N_\mu \equiv \langle 1 \mid \Psi \mid \chi_\mu \rangle$ of the eigenvectors $\mid \chi_\mu \rangle$ are of the order of magnitude

$$N_0 = 1 + O(\epsilon^2), \qquad N_\mu = O(\epsilon) \quad \text{for} \quad \mu > 0. \quad (3)$$

Singular perturbation methods may then be used to obtain a uniformly valid asymptotic solution for $\mid X(t) \rangle$. The result shows that after a short initial transient the dissociation and recombination rate coefficients, k_D and k_R, approach the "steady-state" value

$$k_D = K_{eq} k_R = \lambda_0 [1 + 8(1 - N_0) K_{eq}^{-1} N_A + O(\epsilon^4)], \quad (4)$$

where K_{eq} is the dissociation equilibrium constant. Since this expression depends only on λ_0 and $\mid \chi_0 \rangle$, and since for a given set of initial conditions the incubation time caused by the initial transient may be shown to depend only on $\mid \chi_0 \rangle$, we see that all the important parameters describing the dissociation and recombination of diatomic molecules may be determined from the *lowest* eigenvalue and the corresponding eigenvector. This fact is of immense importance for both analytical and numerical calculations of the rate coefficients and incubation times because, in the limit indicated by Eq. (2), the lowest eigenvalue and the corresponding eigenvector are easily approximated by rapidly convergent iterative techniques.

To show how this may be done, we express the eigenvalue equation (2) in the form $\mid \chi_\mu \rangle = -\lambda_\mu L^{-1} \Psi \mid \chi_\mu \rangle$. If we substitute a trial vector for $\mid \chi_\mu \rangle$ in the right-hand side of this equation and perform the indicated operation, we obtain a first approximation to the eigenvector $\mid \chi_0 \rangle$, within a normalization constant. This first approximation may, in turn, be used as a trial vector to get a second approximation, and so on. After sufficient iterations, the result converges to $\mid \chi_0 \rangle$ with any desired degree of accuracy, in the sense of mean-square error, provided only that the initial trial vector is not orthogonal to $\mid \chi_0 \rangle$.[2] To prove this, we define the nth approximation to the unnormalized eigenvector by the formula $\mid f^{(n)} \rangle = -L^{-1} \Psi \mid f^{(n-1)} \rangle$. Then, since the initial trial vector $\mid f^{(0)} \rangle$ may be expressed in terms of the eigenvectors $\mid \chi_\mu \rangle$ by means of the expansion $\mid f^{(0)} \rangle = \sum_\mu b_\mu \mid \chi_\mu \rangle$, we find that the mean-square error in the normalized eigenvector is

$$E^{(n)} = 2 - 2(\langle f^{(n)} \mid \Psi \mid \chi_0 \rangle / \langle f^{(n)} \mid \Psi \mid f^{(n)} \rangle^{1/2})$$
$$\sim \sum_{\mu > 0} (b_\mu^2 \lambda_0^{2n} / b_0^2 \lambda_\mu^{2n}), \quad (5)$$

which vanishes as $n \to \infty$ provided that $b_0 \neq 0$. A simple approximation to the eigenvalue λ_0 may be obtained from the formula

$$\lambda^{(n)} = \langle f^{(n)} \mid \Psi \mid f^{(n-1)} \rangle / \langle f^{(n)} \mid \Psi \mid f^{(n)} \rangle$$
$$\sim \lambda_0 [1 + \sum_{\mu > 0} (b_\mu^2 \lambda_0^{2n-1} / b_0^2 \lambda_\mu^{2n-1})] \quad (6)$$

which approaches λ_0 as $n \to \infty$ provided that $b_0 \neq 0$.

In the limit indicated by Eq. (2) the calculation converges very rapidly, and only one iteration is necessary. For our initial trial vector we choose the equilibrium distribution $\mid f^{(0)} \rangle = \mid 1 \rangle$. In practice, this usually deviates significantly from $\mid \chi_0 \rangle$ only in the upper energy levels where the weighting function ψ_i is small. The expansion coefficients b_μ are given by the formula $\langle f^{(0)} \mid \Psi \mid \chi_\mu \rangle = N_\mu$. The first approximation to λ_0 is therefore

$$\lambda^{(1)} = - \langle 1 \mid \Psi L^{-1} \Psi \mid 1 \rangle / \langle 1 \mid \Psi L^{-1} \Psi L^{-1} \Psi \mid 1 \rangle$$
$$\sim \lambda_0 [1 + O(\epsilon^4)], \quad (7)$$

where the asymptotic limit follows from Eq. (3). The first approximation to $\mid \chi_0 \rangle$ is

$$\mid \chi^{(1)} \rangle = - L^{-1} \Psi \mid 1 \rangle / \langle 1 \mid \Psi L^{-1} \Psi L^{-1} \Psi \mid 1 \rangle^{1/2}, \quad (8)$$

which, in view of Eq. (3), has a mean-square error $E^{(1)} = O(\epsilon^6)$. Of course, the relative error in the second-order quantity $(1 - N_0)$ is somewhat larger. Nevertheless, we readily find that $(1 - N^{(1)}) = (1 - N_0)[1 + O(\epsilon^2)]$, which is consistent with the accuracy of Eq. (4).

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Ground-State Wavefunctions and Energies for the Helium Isoelectronic Series through Z = 10*

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The method of configuration interaction with a truncated complete set of functions and one variable scale parameter which was recently applied to the first four members of the helium isoelectronic series[1] has been extended to this series through $Z = 10$. The energies obtained for $Z \geq 5$ are lower than have previously been obtained with a configuration-interaction approach,[2] and differ from those obtained with Hylleraas-type functions[3] by 0.002% for $Z = 5$ and by 0.0007% for $Z = 10$. It is found that for $Z \geq 2$ there is a finite range of values of the scale parameter near the energy minimum over which the energy varies by less than 0.00001 a.u., which is the limit of the precision used in the matrix diagonalization.

TABLE I. Ground-state energies for the helium isoelectronic series (in atomic units).

Z	k		E_{calc}	E_{exact}[a]	Error
2	3.17	3.21	−2.90335[b]	−2.90372	0.00037
3	5.09	5.15	−7.27945[b]	−7.27991	0.00046
4	6.88	7.03	−13.65504[b]	−13.65557	0.00053
5	8.70	8.90	−22.03041	−22.03097	0.00056
6	10.40	10.75	−32.40565	−32.40625	0.00060
7	12.10	12.50	−44.78082	−44.78145	0.00063
8	13.75	14.25	−59.15595	−59.15660	0.00065
9	15.50	16.00	−75.53105	−75.53171	0.00066
10	17.25	17.75	−93.90614	−93.90681	0.00067

[a] See Ref. 3.
[b] See Ref. 1.

In Table I are shown the results obtained with the 120-term expansion

$$\Psi_{^1S} = \sum_{n_1=1}^{8} \sum_{n_2=1}^{n_1} \sum_{l=0}^{n_2-1} C(n_1, n_2, l) \Phi_{^1S}(n_1, n_2, l),$$

in which each configuration is the appropriate anti-symmetrized combination of products of the denumerably complete[4] set of single-particle functions,

$$\psi_{nlm}(\xi, \theta, \phi) = \frac{[\Gamma(n-l)]^{1/2}}{[\Gamma(n+l+1)]^{3/2}} \xi^l$$

$$\times \exp(-\xi/2) L_{n-l-1}^{2l+1}(\xi) Y_l^m(\theta, \phi),$$

of the scaled variable $\xi = 2k\mathbf{r}$. The two values of the scale parameter k shown in Table I are the limits of the range of k over which the energy varies by less than 0.00001 a.u.

Since it is the wavefunction, or the approximate solution to the Schrödinger equation, which is ultimately of interest, the behavior of the wavefunction near the energy minimum was studied by calculating the expectation value $\langle r^2 \rangle = \frac{1}{2} \langle (r_1^2 + r_2^2) \rangle$ over the range of scale parameter for which there is no significant change in

TABLE II. Expectation value $\langle r^2 \rangle$ for two-electron atoms (atomic units).

Z	Present work		Scherr and Knight[a]
2	1.1903	1.1950	1.19234
3	0.44588	0.44601	0.44624
4	0.23196	0.23214	0.23206
5	0.14192	0.14198	0.14196
6	0.095712	0.095725	0.095739
7	0.068889	0.068895	0.068904
8	0.051946	0.051951	0.051955
9	0.040565	0.040568	0.040570
10	0.032552	0.032554	0.032556

[a] See Ref. 5.

the energy. The maximum and minimum values obtained are shown in Table II, and compared with the sixth-order perturbation calculation of Scherr and Knight.[5] This expectation value was chosen for several reasons. It is the one property, other than the energy, of an atom in a ^1S state which can be obtained directly from the wavefunction and which can be related to an experimentally measured quantity, in this case the magnetic susceptibility.[6] It has been calculated for $Z=2$ by many different methods,[7] not all of which are based on the energy criterion. A comparison with these other calculations as well as with the experimental value is shown in Table III. Finally, the dominant contribution to this expectation value comes from a significantly different region in space than that which furnishes the dominant contribution to the energy. The agreement shown in Tables II and III provides assurance that the minimum energy is not being obtained at the expense of the spatial behavior of the trial func-

TABLE III. Comparison of the expectation value $\langle r^2 \rangle$ for the ground state of He obtained by various methods.

$\langle r^2 \rangle$	Method	Author
1.192	Configuration interaction	Present work
1.19234	Variation perturbation	Scherr and Knight[a]
1.1930	Stochastic wavefunction	Kalos[b]
1.193475	Hylleraas-type wavefunction	Chung and Hurst[b]
1.193483	Hylleraas-type wavefunction	Pekeris[b]
1.19	Experimental value from magnetic susceptibility[c]	

[a] See Ref. 5.
[b] See Ref. 7.
[c] Handbook of Chemistry and Physics (Chemical Rubber Publ. Co., Cleveland, Ohio, 1966), p. E-103.

tion, and in fact is somewhat better than might be expected from a wavefunction which gives the energy to four or five significant figures. Because of this it seems likely that this type of wavefunction should be quite useful for calculating transition probabilities and other properties of these ions obtainable from oscillator strengths, and this work is now in progress.

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