

TABLE I. For each ion-gas system studied, we give the accuracy of the experimental data displayed in Figs. 1 and 2, along with the values of the parameters $(v_d)_0$ and γ_∞ used in the GER calculations of ND_L . The parameter A^* is set equal to 1.2 for each of the ion-gas systems. The units of $(v_d)_0$ are 10^4 cm/sec, while γ_∞ and A^* are dimensionless.

Ion-gas system	$(v_d)_0$	γ_∞	Accuracy
Cl ⁻ -Ne	0.441	-0.075	$\begin{cases} +12\%, -20\% & 0 \leq E/N \leq 80 \text{ Td} \\ \pm 12\% & E/N > 80 \text{ Td} \end{cases}$
Cl ⁻ -Ar	8.34	-0.050	$\begin{cases} +15\%, -25\% & 0 \leq E/N \leq 100 \text{ Td} \\ \pm 15\% & E/N > 100 \text{ Td} \end{cases}$
Cl ⁻ -Kr	7.15	-0.022	$\pm 12\%$ all E/N
Cl ⁻ -Xe	7.87	-0.0087	$\pm 12\%$ all E/N

soon be submitted for publication. The details of the calculational technique have been reported elsewhere.³ The quantities $(v_d)_0$ and γ_∞ used in the calculation are given in Table I, along with the experimental accuracy. The results of the GER calculation are shown in Figs. 1 and 2 as solid curves.

Agreement between the GER results and the experimental data is considered to be good. These data are somewhat less accurate than those reported earlier for alkali ions because of the present, less favorable,

method of ion production. No experimental data from other laboratories on the diffusion of Cl⁻ ions appear to be available for comparison.

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Pseudo-eigenvalue equation for natural orbitals of two-electron systems and long range behavior

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From the variational principle and the natural orbital¹ (NO) canonical form²⁻⁵ of the wave function of a two-electron singlet system,

$$\psi = \sum_{i=1}^N c_i \chi_i(\mathbf{r}_1) \chi_i(\mathbf{r}_2) (\alpha\beta - \beta\alpha) / \sqrt{2}, \quad (1)$$

we derive a pseudo-eigenvalue equation [Eq. (8)] for the NO's χ_i , which we then use to discuss the long range behavior of the χ_i [Eqs. (12) and (15)].

In Eq. (1) we take the c_i and χ_i to be real, and N to be either finite or infinite. The energy expectation value is then

$$E = \left(\sum_i^N c_i^2 2h_{ii} + \sum_i^N \sum_j^N c_i c_j K_{ij} \right) / \sum_i^N c_i^2 \quad (2)$$

$$= \sum_i^N c_i \langle \chi_i | 2c_i h + \sum_j^N c_j K^{\dagger} | \chi_i \rangle / \sum_i^N c_i^2, \quad (3)$$

where

$$h_{ii} = \langle \chi_i | h | \chi_i \rangle, \quad K_{ij} = \langle \chi_i | K^{\dagger} | \chi_j \rangle,$$

and where

$$h = -\frac{1}{2}\nabla^2 + V = -\frac{1}{2}\nabla^2 - Z/r \text{ (for helium)}, \quad (4)$$

$$\langle \chi_i | K^{\dagger} | \chi_j \rangle = \langle \chi_i(\mathbf{r}_1) \chi_i(\mathbf{r}_2) | 1/r_{12} | \chi_j(\mathbf{r}_1) \chi_j(\mathbf{r}_2) \rangle. \quad (5)$$

To obtain the pseudo-eigenvalue equation, we first vary c_j ,

$$\delta E = 2\delta c_i \langle \chi_i | 2c_i h + \sum_j^N c_j K^{\dagger} - E c_i | \chi_i \rangle / \sum_i^N c_i^2 = 0. \quad (6)$$

We next vary the NO's, preserving the canonical form (1) by simultaneously varying two NOs: $\chi_i \rightarrow \chi_i + \epsilon \chi_j$; $\chi_j \rightarrow \chi_j - \epsilon \chi_i$;

$$\delta E = (c_i - c_j) 4\epsilon \langle \chi_j | (c_i + c_j) h + \sum_i^N c_i K^{\dagger} | \chi_i \rangle = 0. \quad (7)$$

With $c_i - c_j \neq 0$ or with appropriate unitary transformation of degenerate χ_i leaving ψ and $\sum c_i K^i$ invariant, the matrix element in Eq. (7) can be made to vanish, which makes Eqs. (6) and (7) equivalent to the pseudoeigenvalue equation,

$$F\chi_i = (hP + Ph + K)\chi_i = EP\chi_i = \epsilon_i \chi_i, \quad (8)$$

where

$$\epsilon_i = E c_i, \quad P = \sum_i c_i |\chi_i\rangle\langle\chi_i|, \quad \text{and} \quad K = \sum_i c_i K^i. \quad (9)$$

If N is finite, then $c_i = 0$ for $i > N$, and Eq. (8) need hold only for the occupied NO's, not the virtual NO's (cf. the Hartree-Fock case).

In principle, Eqs. (8) and (9) can bypass the "CI" step in an iterative solution, with E and c_i obtained from $E = (\sum_i^N \epsilon_i^2)^{1/2}$, and $c_i = \epsilon_i/E$.

The Fock operator quadratic in the c_i , derived by Ahlrichs, Kutzelnigg, and Bingel⁶ and by Silver, Mehler and Ruedenberg,⁷ is the anticommutator of our F and P , followed by a level shift:

$$F_{\text{NO}}(\text{AKB-SMR}) = FP + PF - 2 \sum_i^N c_i^2 h_{ii} |\chi_i\rangle\langle\chi_i|. \quad (10)$$

We note that $K^i \chi_i \sim (1/r)\chi_i$, and that $K^i \chi_i = O(r^{-2}\chi_i)$ for $i \neq t$, and so to obtain an asymptotic version of Eq. (8) for helium, we drop all terms of order $r^{-2}\chi_i$. We anticipate from the ideas of Morrell, Parr, and Levy,^{8,9} Ahlrichs,¹⁰⁻¹³ Hoffmann-Ostenhof and Hoffmann-Ostenhof,¹⁴ Tal,¹⁵ and Handy, Marron, and Silverstone¹⁶ an asymptotic form, $\chi_i \sim k_i r^\beta e^{-\zeta r} + a_i r^{\beta-1} e^{-\zeta r}$, which we substitute into the asymptotic version of Eq. (8) to determine ζ , β , and k_i . Suppressing the angular variables Θ and ϕ , we obtain

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} \frac{d}{dr} - \frac{Z}{r} + \frac{1}{r} - E\right) c_i (k_i + a_i/r) r^\beta e^{-\zeta r} + \sum_j^N c_j (k_j + a_j/r) h_{ji} r^\beta e^{-\zeta r} = \left\{ \left[\left(-\frac{1}{2}\zeta^2 - E\right) c_i k_i + \sum_j^N c_j k_j h_{ji} \right] + r^{-1} \left[(\zeta\beta + \zeta - Z + 1) c_i k_i + \left(-\frac{1}{2}\zeta^2 - E\right) a_i c_i + \sum_j^N a_j c_j h_{ji} \right] + O(r^{-2}) \right\} r^\beta e^{-\zeta r} \sim 0, \quad (i=1, 2, \dots, N). \quad (11)$$

For Eqs. (11) to hold for $i=1, 2, \dots, N$, the vector $(c_1 k_1, c_2 k_2, \dots, c_N k_N)$ must be an eigenvector of (h_{ji}) , $\sum_j^N c_j k_j h_{ji} = \mu c_i k_i$, where μ is the energy of He^+ computed in the basis $\{\chi_i\}$, $\mu - E$ is the ionization potential of He , and ζ , β , k_i , and a_i are given by

$$\frac{1}{2}\zeta^2 = \mu - E, \quad \beta = (Z - 1 - \zeta)/\zeta, \quad (12)$$

$$k_i = M \langle 1_{\text{SH}^+} | \chi_i \rangle / c_i, \quad a_i = A k_i.$$

M and A are independent of i , but not necessarily of N .

That $k_i = 0$ if χ_i has $l \geq 1$ is indicative of a more rapid fall off. We rewrite ψ with the angular factors of the χ_i explicit,

$$\psi = \sum_{l=0}^L \sum_{\nu=1}^{n_l} d_{\nu l} \mathcal{R}_{\nu l}(r_1) \mathcal{R}_{\nu l}(r_2)$$

$$\times \sum_{m=-l}^l Y_l^m(\theta_1, \phi_1) Y_l^m(\theta_2, \phi_2) (\alpha\beta - \beta\alpha) / \sqrt{2}. \quad (13)$$

For $l > 0$, $\mathcal{R}_{\nu l}$ is coupled asymptotically to the $\mathcal{R}_{\nu 0}$ by the exchange terms in Eq. (8). Setting $\chi_i = \mathcal{R}_{\nu l} Y_l^m$ and keeping the leading exchange term when $l > 0$, we obtain

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} \frac{d}{dr} - \frac{Z-1}{r} - E\right) d_{\nu l} \mathcal{R}_{\nu l} + \sum_{\nu'}^{n_l} d_{\nu'} \mathcal{R}_{\nu'} \mathcal{R}_{\nu l} h_{\nu' \nu l} + (1 - \delta_{l0}) \sum_{\nu'}^{n_0} d_{\nu'} \mathcal{R}_{\nu'} \frac{\langle \mathcal{R}_{\nu' 0} | r^l | \mathcal{R}_{\nu l} \rangle}{2l+1} r^{-l-1} \mathcal{R}_{\nu' 0} \sim 0, \quad (14)$$

which admits the asymptotic solution

$$\mathcal{R}_{\nu 0} \sim k_{\nu 0} r^\beta e^{-\zeta r}, \quad \mathcal{R}_{\nu l} \sim k_{\nu l} r^{\beta-l-1} e^{-\zeta r} (l > 0). \quad (15)$$

As before, the vector $(d_{10} k_{10}, d_{20} k_{20}, \dots, d_{n_0 0} k_{n_0 0})$ is an eigenvector of $(h_{\nu' 0, \nu 0})$, and $k_{\nu 0}$, β and ζ are given by Eqs. (12). For $l > 0$, Eqs. (14) yield simultaneous linear inhomogeneous algebraic equations for the $d_{\nu l} k_{\nu l}$. Since

$$\sum_{m_l} K^{\nu l} \mathcal{R}_{\nu l} Y_l^m \sim r^{-l-1} \mathcal{R}_{\nu l} Y_l^m,$$

the exchange terms omitted from Eq. (14) vanish at least r^{-1} faster than the terms kept.

The derivation is valid for finite N . For infinite N we cannot justify interchanging the two limit processes,

$$\lim_{N \rightarrow \infty} \sum_j^N c_j \chi_j h_{ji}$$

and $\chi_j \sim k_j r^\beta e^{-\zeta r}$, as pointed out by Ahlrichs.¹³ Indeed, an interesting counter example from Eq. (12) is

$$4\pi^{-(1/2)} e^{-Zr} = \lim_{N \rightarrow \infty} \sum_j^N c_j k_j \chi_j / \left(\sum_i^N c_i^2 k_i^2 \right)^{1/2}.$$

Yet for every finite N , each $\chi_j \sim r^\beta e^{-\zeta r}$ with $\zeta \neq Z$, $\beta \neq 0$.

The asymptotic behavior is numerically verifiable. Recent NO analysis of an extensive piecewise polynomial CI wave function¹⁷ for helium clearly shows¹⁸ the qualitative squeeze implied by an r^β factor at $r=0$ and an $r^{-l-1+\delta_{l0}}$ factor at $r=\infty$, and it tends to give quantitative support to Eq. (15). But because of the lack of precision in determining the outer parts of the wave function, the evidence is not definitive.

Note added in proof: Equations not emphasizing the pseudoeigenvalue-equation character of Eqs. (8) and (9), but otherwise quite similar, have been given previously [R. Ahlrichs and F. Driessler, *Theor. Chim. Acta* **36**, 275 (1975), especially Eqs. (14) and (17)-(19)]. Extension into a self-consistent direct method has recently been given [R. Ahlrichs, "Many body perturbation calculations and coupled electron pair models," *Comput. Phys. Commun.* (in press), especially Sec. E]. The authors wish to thank Professor Ahlrichs for a preprint of this work and for helpful remarks.

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Detailed balance in quasiclassical trajectory calculations of thermal rate constants for chemical reactions

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In quasiclassical trajectory (QCT) calculations the collision partners are assigned quantized values of the initial vibrational and rotational energies.^{1,2} The classical equations of motion are then integrated, and the calculated final distributions of vibrational and rotational energy are continuous. Thus these final energies differ from the discrete initial energies of a QCT calculation on the reverse reaction. Thus the QCT method does not satisfy detailed balance, i.e., $k_f/k_r \neq K_{eq}$ where k_f and k_r are calculated equilibrium rate constants for the forward and reverse reactions, and K_{eq} is the equilibrium constant for the reaction. Although the lack of detailed balance in the QCT method is well known,^{2,3} no quantitative comparisons of k_f/k_r have been reported.⁴ We report here a set of such comparisons.

The first is for the endothermic collinear reaction $H_2 + I \rightleftharpoons H + HI$ using a rotated Morse curve potential energy surface⁵ developed earlier. We have already reported⁶ two kinds of calculation of k_f for this system; one calculation (QCT) was standard, but for the other one

[QCT(QM)] we set the reaction probability equal to zero for energies below the product zero-point energy, i.e., below the quantum mechanical threshold. We also reported⁶ some results for the forward reaction as obtained by the QCT reverse histogram method. We have now calculated enough additional trajectories for the reverse reaction to calculate a complete standard QCT rate constant for it. The results are given in Table I where they are compared with accurate quantal results. The error in the QCT rate constant for the reverse reaction decreases from 8% at 300 °K to 1% at 1500 °K. The large error in k_f for this reaction when the quantum mechanical threshold is not enforced has already been discussed⁶; this large error causes k_f/k_r to be 19 times too large at 300 °K, decreasing to 40% too large at 1500 °K. Using the correct quantum mechanical threshold decreases the error in k_f/k_r to 37% at 300 °K and 5% at 1500 °K.

Because an error in k_f/k_r automatically implies a comparable error in k_f or k_r or both, a test of k_f/k_r can be very useful for a three-dimensional reaction for which

TABLE I. Rate constants, rate constant ratios, and equilibrium constants for the collinear reactions $H_2 + I \rightleftharpoons H + HI$.^a

T (°K)	QCT			QCT(QM)		Accurate quantal		
	k_f	k_r	k_f/k_r	k_f	k_f/k_r	k_f	k_r	K_{eq}
300	1.00(-18) ^b	6.24(4)	1.61(-23)	3.28(-20)	5.26(-25)	4.79(-20)	5.77(4)	8.30(-25)
400	4.33(-13)	7.19(4)	6.02(-18)	3.79(-14)	5.27(-19)	5.43(-14)	6.80(4)	7.98(-19)
600	2.12(-7)	8.79(4)	2.42(-12)	4.88(-8)	5.55(-13)	6.55(-8)	8.50(4)	7.71(-13)
1000	9.51(-3)	1.13(5)	8.44(-8)	4.58(-3)	4.05(-8)	5.43(-3)	1.11(5)	4.88(-8)
1500	2.46(0)	1.36(5)	1.81(-5)	1.66(0)	1.22(-5)	1.78(0)	1.38(5)	1.29(-5)

^aRate constants in $\text{cm molec}^{-1} \text{sec}^{-1}$; k_f values from Ref. 6 with sums over vibrational states better converged.

^bNumbers in parentheses are multiplicative powers of ten.