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 \( \rho_0 \) and \( \gamma = \alpha + \beta \) used in the GER calculations of \( \text{ND}_1 \). The parameter \( \alpha^+ \) is set equal to 1.2 for each of the ion–gas systems. The units of \( \rho_0 \) are \( 10^4 \text{ cm/sec} \), while \( \gamma \) and \( \alpha^+ \) are dimensionless.

<table>
<thead>
<tr>
<th>Ion–gas system</th>
<th>( \rho_0 )</th>
<th>( \gamma )</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl–Ne</td>
<td>0.441</td>
<td>-0.075</td>
<td>( \pm 12% ), ( \pm 20% ) 0 ( \leq E/N \leq 80 \text{ Td} )</td>
</tr>
<tr>
<td>Cl–Ar</td>
<td>8.34</td>
<td>-0.050</td>
<td>( \pm 15% ), ( \pm 25% ) 0 ( \leq E/N \leq 100 \text{ Td} )</td>
</tr>
<tr>
<td>Cl–Kr</td>
<td>7.15</td>
<td>-0.022</td>
<td>( \pm 15% ) ( E/N &gt; 100 \text{ Td} )</td>
</tr>
<tr>
<td>Cl–Xe</td>
<td>7.87</td>
<td>-0.0057</td>
<td>( \pm 15% ) ( E/N &gt; 100 \text{ Td} )</td>
</tr>
</tbody>
</table>

soon be submitted for publication. The details of the calculation technique have been reported elsewhere. The quantities \( \rho_0 \) and \( \gamma \) 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 less favorable, method of ion production. No experimental data from other laboratories on the diffusion of Cl ions appear to be available for comparison.

\*Research supported by the Office of Naval Research and the Army Research Office. Approved for public release; distribution unlimited.


2See Ref. 1, Chap. 1.


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

Harris J. Silverstone and Dennis P. Carroll

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

Robert Melville Metzger

Department of Chemistry, The University of Mississippi, University, Mississippi 38677

(Received 20 February 1979)

From the variational principle and the natural orbital1 (NO) canonical form2–3 of the wave function of a two-electron singlet system,

\[ \psi = \sum_{i=1}^{N} c_i \chi_i(x_1, x_2) / \sqrt{2}, \]  

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

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

\[ E = \left( \sum_{i=1}^{N} \chi_i^2 h_{ii} + \sum_{i=1}^{N} \sum_{j=1}^{N} c_i c_j K_{ij} \right) / \sum_{i=1}^{N} \chi_i^2, \]

where

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

and where

\[ h = -\frac{1}{2} \nabla^2 + V = -\frac{1}{2} \nabla^2 - Z/r \] (for helium),

\[ \langle \chi_i | K^{\dagger} | \chi_j \rangle = \langle \chi_i (x_1, x_2) | 1/\gamma_1 | \chi_j (x_1, x_2) \rangle . \]

To obtain the pseudo-eigenvalue equation, we first vary \( c_i \),

\[ 5E = 2\sum_{i=1}^{N} \sum_{j=1}^{N} c_i c_j K_{ij} - 5E \chi_i^2 / \sum_{i=1}^{N} \chi_i^2 = 0. \]

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

\[ 5E = (c_i - c_j) 4\epsilon \chi_i (c_i + c_j) h + \sum_{i=1}^{N} c_i K^{\dagger} | \chi_i \rangle = 0. \]
With \( c_i - c_i' \neq 0 \) or with appropriate unitary transformation of degenerate \( \chi_l \) leaving \( \phi \) and \( \sum c_i K^l \) invariant, the matrix element in Eq. (7) can be made to vanish, which makes Eqs. (6) and (7) equivalent to the pseudoeigenvalue equation,

\[
F_4 \chi_i = (kP + Ph + K) \chi_i = E \chi_i = \epsilon_i \chi_i ,
\]

where

\[
\epsilon_i = E c_i , \quad P = \sum_1^N c_i \chi_i \chi_i ^* , \quad K = \sum_1^N c_i K^l ,
\]

(8)

If \( N \) is finite, then \( c_i = 0 \) for \( i > N \), and Eqs. (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 "CT" step in an iterative solution, with \( \epsilon_i \) and \( c_i \) obtained from

\[
E = \sum_1^N c_i \epsilon_i , \quad \text{and} \quad \epsilon_i = \epsilon_i / E .
\]

The Fock operator quadratic in the \( c_i \) derived by Ahlrichs, Kutzelnigg, and Bingel and by Silver, Mehler and Ruedenberg, is the anticommutator of our \( F \) and \( P \), followed by a level shift,

\[
F_{\text{NO}} (\text{AKB–SMR}) = FP + PF - 2 \sum_1^N c_i^2 \chi_i \chi_i ^* .
\]

(10)

We note that \( K \chi_i = (1/r) \chi_i , \) and that \( K^l \chi_i = O(r^2 \chi_i) \) for \( i > l \), and so to obtain an asymptotic version of Eqs. (8) for helium, we drop all terms of order \( r^{-3} \chi_i ) . \) We anticipate from the ideas of Morrell, Parr, and Levy, Ahlrichs, Hoffmann–Ostenhof and Hoffmann–Ostenhof, Tal, Handy, Marron, and Silverstone an asymptotic form, \( \chi_i \rightarrow r^{-1} e^{-\xi r} + a_i r^{-1} e^{-\xi r} \), which we substitute into the asymptotic version of Eqs. (6) to determine \( \xi \), \( \beta \), and \( k_i \). Suppressing the angular variables \( \phi \) and \( \psi \), we obtain

\[
\epsilon_i = \epsilon_i / E \]  

\[
\begin{align*}
\left( 1 - \frac{d^2}{2 dr^2} - \frac{2}{r} \frac{d}{dr} - \frac{2}{r} - \frac{1}{E} \right) c_i (k_i + a_i \phi) r^\beta e^{-\xi r} \\
+ \sum_1^N c_i (k_i + a_i \phi) k_j r^\beta e^{-\xi r} \\
+ \frac{1}{2} \left[ \frac{1}{a_i} \right] r^\beta e^{-\xi r} - 0, \quad (i = 1, 2, \ldots, N) .
\end{align*}
\]

(11)

For Eqs. (11) to hold for \( i = 1, 2, \ldots, N \), the vector \( (c_1 k_1, c_2 k_2, \ldots, c_N k_N) \) must be an eigenvector of \( (h_{11}) \),

\[
\sum_1^N c_i k_j \chi_i \chi_j ^* = \mu c_i \chi_i \chi_i ^* , \quad \text{where} \quad \mu = \text{the energy of He} ,
\]

computed in the basis \( \{ \chi_i \} \), \( -E \) is the ionization potential of He, and \( \xi \), \( \beta \), \( k_i \), and \( a_i \) are given by

\[
\begin{align*}
\frac{1}{2} \xi^2 & = \mu - E , \\
\beta & = (Z - 1 - \xi) / \xi , \\
k_i & = M (1 + s_{\chi_i}^e) / c_i , \\
a_i & = A k_i .
\end{align*}
\]

(12)

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

That \( k_i = 0 \) if \( i \) has \( l \geq 1 \) is indicative of a more rapid fall off. We rewrite \( \psi \) with the angular factors of the \( \chi_i \) explicit,

\[
\psi = \sum_{l=0}^L d_{l,\alpha} \phi_{\alpha} (r_l) \theta_{\alpha} (\phi_l)
\]

\[
\times \sum_{m=1}^L Y_\ell^m (\phi_1, \theta_1) Y_\ell^m (\phi_2, \theta_2) (\alpha \beta - \alpha \beta) / \sqrt{2} .
\]

(13)

For \( l > 0 \), \( \psi_{\alpha \beta} \) is coupled asymptotically to the \( \alpha \beta \) by the exchange terms in Eq. (8). Setting \( \chi_i = \delta_{i0} Y_0^0 \) and keeping the leading exchange term when \( l > 0 \), we obtain

\[
( - \frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} \frac{d}{dr} - \frac{2}{r} - \frac{1}{r} - E ) d_{l,0} \psi_{l,0} + \sum_{m=1}^l d_{l,0} \psi_{m,0} k_{m,0} \psi_{l,0} \]

\[
+ (1 - 2l) \frac{1}{2l+1} d_{l,0} \psi_{l,0} / \psi_{l,0} = 0 ,
\]

(14)

which admits the asymptotic solution

\[
\psi_{l,0} \approx k_{l,0} r^l e^{-\xi r} , \quad \psi_{l,0} = k_{l,0} r^{l-1} e^{-\xi r} \quad (l > 0).
\]

(15)

As before, the vector \((d_{10} \delta_{10}, d_{20} \delta_{20}, \ldots, d_{N0} \delta_{N0})\) is an eigenvector of \((h_{11})_{\alpha \beta}(\psi_l), \) and \( k_{l,0} \) and \( \beta \) are given by Eqs. (12). For \( l > 0 \), Eqs. (14) yield simultaneous linear inhomogeneous algebraic equations for the \( d_{l,0} \psi_{l,0} \). Since

\[
\sum_{l=0}^N \psi_{l,0} = 0 ,
\]

the exchange terms omitted from Eq. (14) vanish at least \( r^i \) faster than the terms kept.

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

\[
\lim_{N \to \infty} \sum_{l=0}^N c_i \psi_{l,0} = 0 ,
\]

and \( \chi_i \rightarrow r^{-1} e^{-\xi r} \), as pointed out by Ahlrichs. Indeed, an interesting counter example from Eq. (12) is

\[
4^{-1/2} / 2 e^{-\xi r} \approx \lim_{N \to \infty} \sum_{l=0}^N c_i / \left( \sum_{l=0}^N c_i^2 \right)^{1/2} .
\]

(16)

Yet for every finite \( N \), each \( \chi_i \rightarrow r^{-1} e^{-\xi r} \) with \( \xi \neq Z, \beta \neq 0 \).

The asymptotic behavior is numerically verifiable. Recent NO analysis of an extensive piecewise polynomial CI wave function for helium clearly shows the qualitative squeeze implied by an \( r^i \) factor at \( r = 0 \) and an \( r^{-1} e^{-\xi r} \) 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.

The authors wish to thank Dr. David M. Silver for helpful discussions. They also wish to thank Professor Ernest R. Davidson for helpful remarks and for calling their attention to his discussion of systems of equations satisfied by helium natural orbitals, and of various implications of those equations.
Detailed balance in quasiclassical trajectory calculations of thermal rate constants for chemical reactions

Joni C. Gray, Bruce C. Garrett, and Donald G. Truhlar

Chemical Dynamics Laboratory, Kolthoff and Smith Halls of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455
(Received 2 February 1979)

In quasiclassical trajectory (QCT) calculations the collision partners are assigned quantized values of the initial vibrational and rotational energies. 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, no quantitative comparisons of \( k_f/k_r \) have been reported. We report here a set of such comparisons.

The first is for the endothermic collinear reaction \( H_2 + I = H + HI \) using a rotated Morse curve potential energy surface developed earlier. We have already reported 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 reported 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 quantum 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 discussed; 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 3% 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 \( H_2 + I = H + HI \). |
|---|---|---|---|---|---|---|---|
| \( T \) (K) | \( k_f \) | \( k_r \) | \( k_f/k_r \) | \( k_f/k_r \) | \( k_f/k_r \) | \( K_{eq} \) |
| 300 | 1.00(−13) \( b \) | 6.24(4) | 1.61(−13) | 3.28(−20) | 5.26(−25) | 4.78(−20) | 6.77(4) | 5.30(−25) |
| 400 | 4.33(−13) | 7.19(4) | 6.02(−13) | 3.79(−14) | 5.27(−19) | 5.45(−14) | 6.80(4) | 7.98(−19) |
| 600 | 2.12(−7) | 8.79(4) | 2.52(−12) | 4.88(−8) | 5.55(−13) | 6.55(−8) | 8.50(4) | 7.73(−13) |
| 1000 | 9.51(−3) | 1.15(3) | 8.44(−8) | 4.59(−3) | 4.08(−8) | 5.43(−3) | 1.11(5) | 4.88(−8) |
| 1500 | 2.46(0) | 1.36(3) | 1.81(−5) | 1.66(0) | 1.22(−5) | 1.73(0) | 1.38(5) | 1.29(−5) |

\( a \) Present address: Center for Naval Analyses, Arlington, Virginia 22209.