Theoret. Chim. Acta (Berl.) 33, 169—176 (1974)

Hermitian Operators for Two-Centre Wavefunctions

Thuy T. T. Bui and Geoffrey Hunter

Department of Chemistry, York University, Toronto, Canada

Received August 24, 1973/December 19, 1973

Semi-analytical solutions of the Schrödinger equation for a particle moving in the electrostatic field of two other particles a fixed distance apart, are derived in such a way that the resulting matrix eigenvalue equations contain real symmetric band matrices. Numerical techniques appropriate to the solution of the two simultaneous matrix eigenvalue equations are described; in particular the bisection method is used to determine precisely the significant truncation order of the matrices for a given numerical precision.

Key words: Two center wave functions

1. Introduction

The two-centre problem in wave mechanics [1] arises when the Born-Oppenheimer separation [2, 3] is applied to the internal motion of three electrostatically interacting particles [4, 5]. Most of the previous work has been concerned with obtaining solutions for the specific case of the hydrogen molecule-ion [6–27]. The Schrödinger equation is separable in confocal elliptic co-ordinates [1, 5], and all of the precise calculations have been based upon semi-analytical solution of the separated differential equations by the method of Frobenius. An inherent disadvantage of this procedure is that the differential operators are not in general hermitian [28], so that spurious complex-energy eigenvalues may arise in numerical work, and the algorithmic techniques applicable to hermitian (real symmetric) matrices cannot be used [29]. This has been noted previously [30].

This paper is concerned with the derivation of semi-analytical two-centre Coulomb wavefunctions based upon hermitian differential operators. The general technique to be followed is the hybrid Frobenius-Ritz method described previously [30]. This hybrid method produces a hermitian matrix eigenvalue equation from the algebraic (non-integral) method of Frobenius, by a transformation involving the overlap integrals of the basis functions.

2. Parameterisation

The wave equation for the motion of a particle (mass m_3; charge e_3) in the electrostatic field of two other particles (masses m_1, m_2; charges e_1, e_2) a fixed distance R apart, written in confocal elliptic co-ordinates λ, μ, ω and in μ_2-e'-

Rydberg units [4], separates into three ordinary differential equations:

$$\frac{d^2\Omega}{d\omega^2}+m^2\Omega=0 \qquad 0\leqq\omega\leqq 2\pi\,; \tag{1}$$

$$\frac{\partial}{\partial\lambda}(\lambda^2-1)\frac{\partial\Lambda}{\partial\lambda}+\left\{A-p^2\lambda^2-\frac{m^2}{\lambda^2-1}+R\lambda(1+q)\right\}\Lambda=0 \qquad 1\leqq\lambda<\infty\,; \tag{2}$$

$$\frac{\partial}{\partial\mu}(\mu^2-1)\frac{\partial \mathsf{M}}{\partial\mu}+\left\{A-p^2\mu^2-\frac{m^2}{\mu^2-1}+R\mu(1-q)\right\}\mathsf{M}=0 \quad -1\leqq\mu\leqq+1\,. \tag{3}$$

The separation constants are m and A. q is the charge ratio e_2/e_1. p is related to the energy E by:

$$p=\frac{R}{2}(-E)^{1/2}\,. \tag{4}$$

The proper solutions of (1) are well known (Eq. (5) of [5]).

For bound three-particle states ($E<0$) one of the particles must have the opposite sign of charge from the other two particles, so that without loss of generality in the application of the Born-Oppenheimer separation, the particle labels may be chosen so that e_1e_3 is negative [4]. This is implicit in the μ_2-e'-Rydberg system of units. Thus the charge ratio q may be positive or negative.

The charge ratio q may be restricted to the range $-\infty<q\leqq+1$ by the following considerations. New variables $q', R', E', p', \lambda', \mu'$ may be defined by:

$$q'=1/q\,; \qquad R'=qR\,; \qquad E'=E/q^2\,; \qquad p'=p \tag{5}$$
$$\lambda'=\lambda\,; \qquad \mu'=-\mu\,.$$

Replacement of the original variables by the primed variables according to (5) leads to an identity transformation of Eqs. (2) and (3). Thus the solutions Λ, M, for $|q|\geqq 1$ are related to those for $|q|\leqq 1$. In particular the two principal parameters A and E are related by:

$$A(R,q)=A(qR,1/q)$$
$$E(R,q)=q^2\,E(qR,1/q)\,. \tag{6}$$

The transformation $\mu'=-\mu$ is of no consequence because of the symmetric range of μ, $-1\leqq\mu\leqq+1$. Apparently one could restrict q to the range $-1\leqq q\leqq 1$. However for negative values of q, the transformation (5) changes positive R into negative R'. Thus in order to retain the distance R as a positive parameter, q is allowed the range $-\infty<q\leqq+1$. Thus Eq. (6) are only practically useful for $q>0$.

3. The μ Equation: $q=1$

This special case of $q=1$ is straightforward. Following previous developments [1, 5, 12] $\mathsf{M}(\mu, R)$ is expanded in terms of associated Legendre polynomials $P_k^m(\mu)$ [31] according to Eq. (10) of [5]. Application of Frobenius' method leads to a set of homogeneous linear equations for the coefficients $f_k(R)$ represented by the matrix equation [5, 32]:

$$\boldsymbol{F}\cdot\boldsymbol{f}=A\boldsymbol{f}\,. \tag{7}$$

The elements of the vector $\boldsymbol{f}$ are the coefficients $\{f_k\,;\,k\geqq 0\}$, and $\boldsymbol{F}$ is a tridiagonal matrix, whose elements F_{jk} are given by Eq. (12) of [5] for the case of $q=1$.

It is apparent from this equation in [5] that the matrix $\boldsymbol{F}$ is not symmetric, so that the eigenvalues A of Eq. (7) are not necessarily real. Equation (7) may be

transformed into a symmetric matrix eigenvalue equation through the diagonal overlap matrix $\boldsymbol{S}$ of the Legendre polynomials. The elements of $\boldsymbol{S}$ are given by [31]:

$$S_{kk} = \int_{-1}^{+1} [P^m_{m+s+2k}(\mu)]^2 \, d\mu = \frac{2(2m+s+2k)!}{(s+2k)!\,(2m+2s+4k+1)} \qquad \begin{matrix} k \geqq 0 \\ s = 0 \quad \text{or} \quad 1 \,. \end{matrix} \tag{8}$$

A diagonal square root matrix $\boldsymbol{U}$ is defined to have elements:

$$U_{kk} = [S_{kk}]^{1/2} \,. \tag{9}$$

Equation (7) is transformed into the symmetric tridiagonal matrix eigenvalue equation:

$$\boldsymbol{F}' \boldsymbol{f}' = A \boldsymbol{f}' \tag{10}$$

where $\boldsymbol{F}'$ and $\boldsymbol{f}'$ are defined by:

$$\boldsymbol{F}' = \boldsymbol{U}\,\boldsymbol{F}\,\boldsymbol{U}^{-1} \tag{11}$$

$$\boldsymbol{f}' = \boldsymbol{U}\,\boldsymbol{f} \,. \tag{12}$$

Thus diagonal elements of $\boldsymbol{F}'$ are the same as those of $\boldsymbol{F}$:

$$F_{kk} = F'_{kk} = -(m+s+2k)(m+s+2k+1) + \frac{P^2}{(2m+2s+4k+1)} \left\{ \frac{(s+2k)(2m+s+2k)}{(2m+2s+4k-1)} + \frac{(s+2k+1)(2m+s+2k+1)}{(2m+s+4k+3)} \right\}$$

and the co-diagonal elements of $\boldsymbol{F}'$ are:

$$F'_{kk+1} = F'_{k+1k} = \frac{P^2}{(2m+2s+4k+3)} \cdot \left[\frac{(s+2k+1)(s+2k+2)(2m+s+2k+1)(2m+s+2k+2)}{(2m+2s+4k+1)(2m+2s+4k+5)} \right]^{1/2} \qquad k \geqq 0 \,. \tag{13}$$

The elements of $\boldsymbol{f}'$ are related to those of $\boldsymbol{f}$ by:

$$f'_k = U_{kk} f_k = \left[\frac{2(2m+s+2k)!}{(s+2k)!\,(2m+2s+4k+1)} \right]^{1/2} f_k \tag{14}$$

$s = 0$ or 1 for $\mathsf{M}(\mu, R)$ an even or odd function of μ.

4. The μ Equation: $q \neq 1$

Solutions of Eq. (3) for the general case of $q \neq 1$ have been sought in previous work in one of three forms: [1, 5, 14, 24, 26, 27]. Two of these forms involve a factor $\exp(\pm p\mu)$ in $\mathsf{M}(\mu, R)$. This exponential factor is important in the direct application of Frobenius' method [1, 14, 27] since it leads to a three-term recurrence relation to which the theory of infinite continued fractions [33] may be applied. However the expansions of $\mathsf{M}(\mu, R)$ including the $\exp(\pm p\mu)$ factor lead to a non-sparse overlap matrix, so that they are not suitable for application of the hybrid method. Following previous work [5] the method adopted for $q \neq 1$ is a straightforward expansion of $\mathsf{M}(\mu, R)$ in associated Legendre polynomials (Eq. (10) of [5]). The procedure is similar to that for the case $q = 1$, except that the $\mathsf{M}(\mu, R)$ are no longer even or odd functions of μ, and the term $R\mu(1-q)$ is no longer zero. The $\boldsymbol{F}$ matrix in this case is unsymmetrical and pentadiagonal

(Eq. (12) of [5]). The diagonal overlap matrix $\boldsymbol{S}$ is essentially the same as in the case $q=1$ (Eq. (8)) except that both $s=0$ and $s=1$ elements occur together. The algebraic details of the hybrid method for this case are recorded elsewhere [32]. The resulting symmetric pentadiagonal matrix $\boldsymbol{F}'$ has elements:

$$F'_{kk} = -(m+k)(m+k+1) + \frac{P^2}{(2m+2k+1)}\left\{\frac{k(2m+k)}{(2m+2k-1)} + \frac{(k+1)(2m+k+1)}{(2m+2k+3)}\right\}$$

$$F'_{kk+1} = F'_{k+1k} = R(q-1)\left[\frac{(k+1)(2m+k+1)}{(2m+2k+3)(2m+2k+1)}\right]^{1/2} \tag{15}$$

$$F'_{kk+2} = F'_{k+2k} = \frac{P^2}{(2m+2k+3)}\left[\frac{(k+1)(k+2)(2m+k+1)(2m+k+2)}{(2m+2k+1)(2m+2k+5)}\right]^{1/2} \qquad k \geqq 0\,.$$

The symmetric matrix eigenvalue equation has the same form as (10) with $\boldsymbol{F}'$ given by (15); the elements of $\boldsymbol{f}'$ are related to the coefficients f_k by:

$$f'_k = \left[\frac{2(2m+k)!}{k!\,(2m+2k+1)}\right]^{1/2} f_k\,. \tag{16}$$

5. The λ Equation

Semi-analytical solutions of Eq. (2) have been presented previously by Hylleraas [8] and Jaffé [9]. The first step in both of these solutions is the removal of a factor $(\lambda^2-1)^{m/2}$:

$$\Lambda(\lambda, R) = (\lambda^2-1)^{m/2}\, N(\lambda, R)\,. \tag{17}$$

The differential equation satisfied by $N(\lambda, R)$ is:

$$(\lambda^2-1)\frac{d^2N}{d\lambda^2} + 2(m+1)\lambda\frac{dN}{d\lambda} + [m(m+1) - p^2\lambda^2 + R\lambda(1+q)]N = -AN\,. \tag{18}$$

Jaffé's solution involves an irrational factor $(\lambda+1)^\sigma$, and a power series in $(\lambda-1)/(\lambda+1)$. Thus the overlap integrals cannot be evaluated analytically, and the overlap matrix is non-sparse (no zero elements). Therefore the Jaffé form of semi-analytical solution is not suitable for the application of the hybrid method. It is, however, interesting to note that the equivalence of the Jaffé and Hylleraas expansions has been proved by Helfrich and Hartmann [20].

Hylleraas' solution expands $N(\lambda, R)$ in terms of the associated Laguerre polynomials $L^m_{m+k}(x)$, where the variable x is related to λ by:

$$x = 2p(\lambda-1)\,. \tag{19}$$

This change of independent variable changes the range from $1 \leqq \lambda < \infty$ to $0 \leqq x < \infty$. It also makes the correct asymptotic form of N, $\exp(-p\lambda)$ or $\exp(-x/2)$, the appropriate weighting factor for the Laguerre polynomials. Thus Hylleraas' solution has the form:

$$N = \exp(-x/2)\sum_{k=0}^{\infty} g_k(R)\, L^m_k(x)\,. \tag{20}$$

Substitution of (20) into (18) followed by application of Frobenius' method employing the algebraic properties of the associated Laguerre polynomials L^m_k

[34], leads to a matrix eigenvalue equation [1, 5, 26, 27]:

$$\boldsymbol{G}\cdot\boldsymbol{g} = -A\boldsymbol{g}\,. \tag{21}$$

The elements of the vector $\boldsymbol{g}$ are the coefficients g_k in (20) and the elements of the tridiagonal matrix $\boldsymbol{G}$ are, in our notation:

$$\begin{aligned} G_{kk} &= 2k(\sigma-2p-k)-p^2+m(m+1)+\sigma(m+1+2p)\\ G_{kk+1} &= (k+m+1)(k-m-\sigma)\\ G_{k+1k} &= (k+1)(k-\sigma) \qquad k\geqq 0 \end{aligned} \tag{22}$$

where the parameter σ is defined by:

$$\sigma = \frac{R(1+q)}{2p} - m - 1 = \frac{1+q}{\sqrt{-E}} - m - 1\,. \tag{23}$$

It is apparent from (22) and (23) that when $m=0$ or $q=-1$, the $\boldsymbol{G}$ matrix is symmetric. Thus in these special cases Hylleraas' solution produces a symmetric matrix eigenvalue equation by direct application of Frobenius' method. This circumstance arises when $m=0$ because the Laguerre polynomials are normalised when $m=0$: that is the overlap matrix is simply the unit matrix in this case.

6. The λ Equation: $m>0$ and $q\neq -1$

This case presents a problem somewhat similar to that encountered when the factor $\exp(\pm p\mu)$ is introduced into the solutions $\mathsf{M}(\mu, R)$ of the μ equation when $q\neq 1$ (Section 4). The problem for the λ equation is created by the introduction of the factor $(\lambda^2-1)^{m/2}$ (Eq. (17)). The differential operator in Eq. (18) is only hermitian when $m=0$. The operator may be made hermitian by pre-multiplication by $(\lambda^2-1)^m$ or $[x(x+4p)]^m$. However the associated Laguerre polynomials are not orthogonal with respect to the weighting factor $[x(x+4p)]^m\exp(-x)$, so that they are not the appropriate orthogonal basis functions for the case $m\neq 0$.

After considering possible alternatives we concluded that direct application of the Ritz variational method utilising the Hylleraas expansion (17, 20), is the most suitable procedure for the production of a symmetric matrix eigenvalue equation from the λ equation when $m>0$ and $q\neq -1$. The essential distinction from Frobenius' method is that the orthogonality of the Laguerre polynomials is employed rather than their linear independence [34]:

$$\int_0^\infty \exp(-x)\,x^m\,L_k^m(x)\,L_j^m(x)\,dx = \delta_{kj}\times\frac{(m+k)!}{k!}\,. \tag{24}$$

The general procedure is as follows. The Hylleraas expansion (20) is substituted into (18), and the derivatives of L_k^m and powers of x removed by use of the algebraic properties of the Laguerre polynomials [34] just as in Frobenius' method (Section 5). The resulting equation is then multiplied by $[x(x+4p)]^m\exp(-x/2)$ to make the operator hermitian, so that (18) becomes:

$$\begin{aligned} \exp(-x)\,[x(x+4p)]^m\{&L_k^m[2k(\sigma-2p-k)-p^2+m(m+1)+\sigma(m+1+2p)\\ &+L_{k+1}^m[(k+1)(k-\sigma)]+L_{k-1}^m[(m+k)(k-m-1-\sigma)]\}\\ &=\exp(-x)\,[x(x+4p)]^m\{-AL_k^m\}\,. \end{aligned} \tag{25}$$

This equation is multiplied by L_j^m and integrated $\left(\int_0^\infty dx\right)$. The left hand side of (25) produces the hamiltonian matrix element H_{jk}, and the right hand side the overlap matrix element S_{jk}. The eigenvalue equation is:

$$\boldsymbol{H}\boldsymbol{g} = -A\boldsymbol{S}\boldsymbol{g}\,. \tag{26}$$

The matrices $\boldsymbol{H}$ and $\boldsymbol{S}$ are both symmetric band matrices. The matrix elements H_{jk} and S_{jk} are evaluated by expanding $(x+4p)^m L_j^m$ and subsequent removal of the powers of x by the recurrence relation between the Laguerre polynomials [34]. This procedure is recursive for increasing values of m in the sense that $(x+4p)^{m+1} = (m+4p)(x+4p)^m$. The non-zero matrix elements are then determined by (24).

The overlap matrix $\boldsymbol{S}$ has m *co*-diagonal bands, and the $\boldsymbol{H}$ matrix $m+1$ *co*-diagonal bands, above and below the principal diagonal. Thus the structure of the matrices depends upon m, so that it is not possible to formulate the matrix elements for a general value of m.

7. The λ Equation: $m=1$

For the specific case of $m=1$ the tridiagonal overlap matrix $\boldsymbol{S}$, and the pentadiagonal hamiltonian matrix $\boldsymbol{H}$, have the following elements.

$$\begin{aligned} S_{kk} &= 2(k+1)(2p+k+1) \\ S_{kk+1} &= S_{k+1k} = -(k+1)(k+2) \qquad k \geqq 0 \end{aligned} \tag{27}$$

$$\begin{aligned} H_{kk} &= 2(k+1)\{(2p+k+1)[2+2\sigma(p+k+1)-p^2]+\sigma(k+1)^2 \\ &\quad -k[4p(2p+2k+1)+3k(k+1)]\} \\ H_{kk+1} &= H_{k+1k} = (k+1)(k+2)\{4k(2p+k+1)-[2+2\sigma(2k+3+4p)-p^2]\} \\ H_{kk+2} &= H_{k+2k} = (k+1)(k+2)(k+3)(\sigma-k) \qquad k \geqq 0\,. \end{aligned} \tag{28}$$

Transformation of (26) to the standard eigenvalue form:

$$\boldsymbol{G}'\boldsymbol{g}' = -A\boldsymbol{g}' \tag{29}$$

is best done by the numerical square-root (Choleski) method [35], since despite the sparse structure of $\boldsymbol{H}$ and $\boldsymbol{S}$, the $\boldsymbol{G}'$ matrix is non-sparse. An alternative method has been given recently by Crawford [36].

8. Numerical Techniques

For given values of the parameters q, R, and m, the numerical problem is to solve the two eigenvalue Eqs. (10) and (21) (or (29) if $m>0$ and $q \neq -1$) simultaneously. That is one must find a value of the energy E (upon which the $\boldsymbol{F}'$ and $\boldsymbol{G}'$ matrices depend), such that the required eigenvalue A_μ of (10) is the same as the required eigenvalue A_λ of (21) [or (26)] to the prescribed precision.

The eigenvalues A_μ and A_λ are determined by firstly transforming any non-tridiagonal matrices to symmetric tridiagonal form by Householder's procedure [29, 37]. The required eigenvalues of the tridiagonal matrices are then determined by the bisection procedure [4, 29, 38]. This procedure has the advantage over alternative procedures, that one can specify which eigenvalue is determined. In terms of united atom quantum numbers n, l, m, the required eigenvalue of (21) or (26) is the $(n-l)^{\text{th}}$, and that of Eq. (10) the $(l+1-m)^{\text{th}}$ [5, 12, 17, 27].

The bisection procedure also has the advantage that the numerically significant order of the matrices for the determined eigenvalue is obtained as a secondary result of the calculation [32, 39]. The numerically significant order applies to the eigenvectors $\boldsymbol{g}'$ or $\boldsymbol{f}'$, so that the precise order at which these in principle infinite order vectors should be truncated is determined.

The iteration towards a value of E such that $A_\mu = A_\lambda$ has been described previously [5], with the modification in the light of this new work, that the significant orders of the $\boldsymbol{G}'$ and $\boldsymbol{F}'$ matrices are employed to considerable speed up the iteration procedure. With this modification the computing time involved is comparable with that claimed by Power in some recent computational work based upon the traditional unsymmetrical tridiagonal matrices [27]. The use of symmetric matrices, and the bisection method, has the advantage over previous methods that iteration towards a specific solution n, l, m, for any given value of R, is assured. In previous work one had to change R in small steps, beginning at $R=0$ (or $R \approx \infty$) where E is known analytically. When two potential curves are close together at certain values of R, this traditional method does not always converge to the required solution [5, 27].

In our experience the eigenvectors $\boldsymbol{g}'$ and $\boldsymbol{f}'$ of the tridiagonal matrices can be accurately generated by forward substitution [29, 32]. For this reason, and also because most of the computing time is taken up with iterating towards self-consistent values of A and E (including the iterative bisection procedure), two centre wavefunctions can conveniently be tabulated as self-consistent values of A and E for specified values of the parameters R, q, n, l, m, together with the significant orders of the $\boldsymbol{g}'$ and $\boldsymbol{f}'$ vectors. If the elements of these vectors are required in a subsequent application of the tables, they can easily be computed from the formulae for the $\boldsymbol{F}'$, $\boldsymbol{G}'$ (or $\boldsymbol{H}$) matrix elements. This evaluation of the vector elements is a non-iterative numerical procedure.

9. Convergence of the Expansions

The significant order of the $\boldsymbol{f}'$ vector increases with increasing intercentre distance R. Typically for 12-digit precision in A and E, the significant order of $\boldsymbol{f}'$ will be 3–10 at $R \approx 1$, and 20–40 at $R \approx 50$. Although the significant order of $\boldsymbol{f}'$ is quite large at large values of R, there is no problem in practice of obtaining the required numerical convergence.

Reciprocally the significant order of the $\boldsymbol{g}'$ vector is small at large values of R ($R \approx 50$) and large at smaller values of R ($R \approx 1$). For positive values of q, $\boldsymbol{g}'$ also coverges rapidly at very small values of R ($R \lesssim 0.1$). For negative values of q, and in particular for $q=-1$, the $\boldsymbol{g}$ vector does not really converge for $R \lesssim 1$. This slowly-convergent situation is associated with a tendency for the energy E to approach zero. In particular for $q=-1$, bound states of particle 3 within the dipole field only exist for R larger than certain critical values [25, 40–42]. This slowly-convergent situation is not likely to be a serious problem in applications, because at small values of R for $q<0$, the potential energy between Particles 1 and 2 is dominated by their Coulomb attraction: the contribution from the averaged motion of Particle 3 is relatively small at small values of R.

Acknowledgement. This work was supported by the National Research Council of Canada.

References

1. Baber, W. G., Hassé, H. R.: Proc. Cambridge Phil. Soc. **31**, 564 (1935)
2. Born, M., Oppenheimer, R.: Ann. Physik **84**, 457 (1927)
3. Born, M., Huang, K.: Dynamical theory of crystal lattices (Appendices). Oxford: Clarendon Press 1954
4. Hunter, G., Gray, B. F., Pritchard, H. O.: J. Chem. Phys. **45**, 3806 (1966)
5. Hunter, G., Pritchard, H. O.: J. Chem. Phys. **46**, 2146 (1967)
6. Burrau, O.: K. Danske Vidensk. Selsk. **7**, 1 (1927)
7. Teller, E.: Z. Physik **61**, 458 (1930)
8. Hylleraas, E. A.: Z. Physik **71**, 739 (1931)
9. Jaffé, G.: Z. Physik **87**, 535 (1934)
10. Sandeman, I.: Proc. Roy. Soc. Edinburgh **55**, 72 (1925)
11. Johnson, V. A.: Phys. Rev. **60**, 373 (1941)
12. Bates, D. R., Ledsham, K., Stewart, A. L.: Phil. Trans. Roy. Soc. (London) A **246**, 215 (1953)
13. Wallis, R. G., Hulbert, H. M.: J. Chem. Phys. **22**, 774 (1954)
14. Bates, D. R., Carson, T. R.: Proc. Roy. Soc. A **234**, 207 (1956)
15. Cohen, S., Judd, D. L., Riddell, R. J.: Phys. Rev. **119**, 384, 397 (1960)
16. Cohen, S., Hiskes, J. R., Riddell, R. J.: Phys. Rev. **119**, 1025 (1960)
17. Kotani, M., Ohno, K., Kayama, K.: Handbuch der Physik, Vol. **37/2**, p. 1 (1961)
18. Wind, H.: J. Chem. Phys. **42**, 2371 (1965)
19. Peek, J. M.: J. Chem. Phys. **43**, 3004 (1965)
20. Helfrich, K., Hartmann, H.: Theoret. Chim. Acta (Berl.) **3**, 21 (1965)
21. Bates, D. R., Reid, R. H. G.: Advances in atomic and molecular physics, Vol. **4**. New York: Wiley 1968
22. Coulson, C. A., Joseph, A.: Intern. J. Quant. Chem. **1**, 337 (1967)
23. Hartmann, H., Helfrich, K.: Theoret. Chim. Acta (Berl.) **10**, 406 (1968)
24. Helfrich, K., Hartmann, H.: Theoret. Chim. Acta (Berl.) **16**, 263 (1970)
25. Kehl, S., Helfrich, K., Hartmann, H.: Theoret. Chim. Acta (Berl.) **21**, 44 (1971)
26. Helfrich, K.: Theoret. Chim. Acta (Berl.) **21**, 381 (1971)
27. Power, J. D.: Phil. Trans. Roy. Soc. (London) A **274**, 663 (1973)
28. Margenau, H., Murphy, G. M.: The mathematics of physics and chemistry, Section 11.4. Princeton: van Nostrand 1956
29. Wilkinson, J. H.: The algebraic eigenvalue problem. Oxford: Clarendon Press 1965
30. Hunter, G.: Theoret. Chim. Acta (Berl.) **17**, 216 (1970)
31. Ref. [28], Section 3.6
32. Bui, T. T. T.: Two-centre wave functions; M. Sc. Thesis. Toronto: York University 1971
33. Wall, H. S.: Analytic theory of continued fractions. New York: Chelsea 1967
34. Gradshteyn, I. S., Ryzhik, I. M.: Table of integrals, series, and products. Translated by A. Jeffrey. New York: Academic Press, 1965
35. Fadeev, D. K., Fadeeva, V. N.: Computational methods of linear algebra. San Francisco: Freeman 1963
36. Crawford, C. R.: Comm. A.C.M. **16**, 41 (1973)
37. Wilkinson, J. H., Reinsch, C.: Linear algebra: Handbook for automatic computation, Vol. **II**, p. 212. New York: Springer-Verlag 1971
38. Modern computing methods: Notes on applied science No. 6 from the National Physical Laboratory. London: Her Majesty's Stationery Office 1961
39. Bui, T. T. T., Hunter, G.: The significant order of symmetric tridiagonal matrices. J. Inst. Math. Appl. (in press) 1974
40. Lévy-Leblond, J.-M.: Phys. Rev. **153**, 1 (1967)
41. Coulson, C. A., Walmsley, M.: Proc. Phys. Soc. **91**, 31 (1967)
42. Crawford, O. H.: Proc. Phys. Soc. **91**, 279 (1967)

Professor G. Hunter
Department of Chemistry
York University
4700 Keele Street
Downsview M3J 1P3
Ontario, Canada