Kinetically-balanced Dirac equation: Properties and applications

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Abstract. Properties of the Dirac equation defined in a space restricted by imposing the non-relativistic kinetic balance condition on the small component of the Dirac spinor (referred to as the kinetically-balanced Dirac equation) are analysed. In particular links between the kinetically balanced Dirac equation and the corresponding Schrödinger equation are discussed. It is proposed that the kinetically-balanced Dirac equation may be used as a simple tool to generate basis sets for relativistic calculations from their non-relativistic counterparts.

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1. Introduction

With the formulation by Hall [1] and Roothaan [2] of the method of solving Hartree-Fock equations based on basis-set expansions of orbitals, emerged the problem of an optimum choice of the basis set for the expansion. Over the years two main approaches to the basis set problem developed. One, usually referred to as the *algebraic* approach is based on a systematic generation of basis sets imposing some simple conditions upon the basis functions (as for example selection of the exponents so that they form a geometric progression). A very good review of this approach has recently been given by Wilson [3]. Another, *numerical*, approach is based on a generation of the basis sets from a condition (usually derived from the variational principle) for some model systems (usually for atoms). These basis sets are then tabulated for future applications. There are several reviews of this approach [4, 5] and extensive tabulations [6, 7, 8].

Probably the most general an efficent implementation of the numerical approach in non-relativistic calculations is based on the idea of a simultaneous optimization of both linear and nonlinear parameters in the basis-set-expanded orbitals [9]. In a series of

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recent papers [10, 11, 12] sets of the energetically optimal contracted Gaussian orbitals have been derived by a direct minimization of the Hartree-Fock-type Rayleigh quotient in the space of all parameters (the linear coefficients and the exponents) defining the orbital. The calculations performed for the ground states of all atoms from He through Kr resulted in very high quality contracted Gaussian basis sets.

The problem of selection of an optimum basis set for relativistic calculations is apparently similar to that in the non-relativistic case, however it is much more subtle. An incorrect choosing basis sets in early attempts to solving Dirac-Fock equations [13] resulted in the so called *variational collapse*. The reasons for this behaviour of the algebraic Dirac-Fock equations have been explained in works of Grant *et al.* [14, 15] and of Kutzelnigg [16]. The explanation carried also a prescription on what to do in order to prevent this udesirable phenomenon: the basis set has to fulfill the correct boundary conditions. Though the conditions which are sufficient to prevent the variational collapse in relativistic calculations are easy to formulate, their direct implementation is not always possible. In particular, an incorrect asymptotic behaviour at both nucleus and infinity is inherent for the Gaussian functions, most commonly used in molecular variational calculations. Fortunately there are several theorems which allow us for a safe use of the variational principle also in this case. As proven by Grant [15], if the Gaussian basis is kinetically balanced and if the linear parameters in the expansions of the Dirac-Fock orbitals are the only ones which are varied, then the variational collapse would not appear unless the maximum exponent is larger than a certain (rather large) threshold value. This prescription leads to a straightforward generalization of the non-relativistic parameter-optimization-based approach: take a basis set in which the small component is related to the large one by the kinetic balance condition and minmize the Rayleigh quotient corresponding to a properly selected model Dirac-Fock problem with respect to both linear and non-linear basis set parameters. Unfortunately, the results of this procedure obtained with several-term expansions suffered from the variational collapse already for the medium Z atoms [17]. An analysis of this phenomenon and formulation of an alternative approach is the aim of this paper.

Atomic units are used in this paper. The velocity of light is taken to be $c = 1/\alpha = 137.0359895$.

2. Kinetically balanced Dirac equation

Let us consider a single Dirac electron in a field of a Coulomb-type radial potential U(r). For the time being $U(r)$ may represent any kind of a local atomic potential as e.g. a Dirac-Slater one, any kind of a model potential or simply a hydrogenic Coulomb potential. We assume that the Dirac spinor is selected as

$$\Psi = \begin{pmatrix} \Psi^{\mathrm{L}} \\ \Psi^{\mathrm{S}} \end{pmatrix}, \tag{1}$$

where

$$\Psi^{\mathrm{L}} = \frac{1}{r} A^{\mathrm{L}}(\Omega)\, \Phi^{\mathrm{L}}(r) \;\text{ and }\; \Psi^{\mathrm{S}} = \frac{1}{r} A^{\mathrm{S}}(\Omega)\, \Phi^{\mathrm{S}}(r) \tag{2}$$

are, respectively, large and small components of the wavefunction. The angular and spin parts of the trial functions, $A(\Omega)$, are equal to the exact ones. The radial Dirac equation, for the case under consideration, reads

$$\begin{pmatrix} U(r)-E & c\hat{\mathcal{O}}^\dagger \\ c\hat{\mathcal{O}} & U(r)-2c^2-E \end{pmatrix} \begin{pmatrix} \Phi^{\mathrm{L}} \\ \Phi^{\mathrm{S}} \end{pmatrix} = 0, \tag{3}$$

where

$$\hat{\mathcal{O}} = \frac{\kappa}{r} + \frac{\mathrm{d}}{\mathrm{d}r} \tag{4}$$

is the radial part of $(\boldsymbol{\sigma}\cdot\boldsymbol{p})$ operator (κ is the Dirac angular momentum quantum number, $\boldsymbol{\sigma}$ are the 2×2 Pauli matrices and and $\boldsymbol{p}$ is the momentum operator). As one can easily see,

$$\hat{\mathcal{O}}^\dagger\hat{\mathcal{O}} = -\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{\kappa(\kappa+1)}{r^2} \tag{5}$$

and in the case of $s_{1/2}$ states ($\kappa=-1$) it becomes equal to the negative of the second derivative with respect to r.

According to the kinetic balance condition

$$\Phi^{\mathrm{S}}(r) = \hat{\mathcal{O}}\Phi^{\mathrm{L}}(r). \tag{6}$$

If the small component is determined by this condition then the the Dirac equation (3) becomes

$$\begin{pmatrix} U-E & c\hat{\mathcal{O}}^\dagger \\ c\hat{\mathcal{O}} & U-2c^2-E \end{pmatrix} \begin{pmatrix} C^{\mathrm{L}}\Phi^{\mathrm{L}} \\ C^{\mathrm{S}}\hat{\mathcal{O}}\Phi^{\mathrm{L}} \end{pmatrix} = 0. \tag{7}$$

Equation (7) is referred to as the *kinetically balanced* Dirac equation. Obviously, a kinetically balanced wavefunction cannot be an exact solution of the Dirac equation, except for the free-particle. However the equation may be used as a generator of kinetically balanced basis sets.

Equation (7) may be rewriten as a system of two equations:

$$\left[\frac{1}{2m}\hat{\mathcal{O}}^\dagger\hat{\mathcal{O}} + U - E_m\right]\Phi_m \qquad = 0, \tag{8}$$

$$\left[2m - 2 + \alpha^2 U - \alpha^2 E_m\right]\hat{\mathcal{O}}\Phi_m = 0, \tag{9}$$

where

$$m = \alpha\frac{C^{\mathrm{L}}}{2C^{\mathrm{S}}} \tag{10}$$

and Φ_m stands for Φ^{L} normalized to unity. The first of them is identical to the Schrödinger equation for a particle with an effective mass m. The second equation cannot be fulfilled if U is a function of r. Then, the best we can do is to convert it to a relation between the expectation values which is appropriate for determining m in equation (8). By mutiplying equation (9) by $(\hat{\mathcal{O}}\Phi_m)^\dagger$ and integrating over r we obtain

$$2T_m(2m - 2 - \alpha^2 E_m) + \alpha^2 X_m = 0, \tag{11}$$

where $\Omega_m = \langle \Phi_m | \hat{\Omega} | \Phi_m \rangle$. If we introduce a new variable $\rho = mr$ then one can easily see that

$$E_m = m\, E_1, \quad T_m = m\, T_1, \quad X_m = m^2\, X_1 \tag{12}$$

and

$$m = \frac{1}{1+\delta}, \quad \text{where} \quad \delta = \frac{\alpha^2}{4}\left(\frac{X_1}{T_1} - 2\, E_1\right). \tag{13}$$

If $U = -\frac{Z}{R}$ (the hydrogenic potential), then $\Phi_m(r)$ is the hydrogenic radial wavefunction,

$$E_1 = -\frac{Z^2}{2n^2}, \quad V_1 = 2E_1, \quad T_1 = -E_1, \quad X_1 = -\frac{Z^4}{n^4}\left(\frac{2n}{|\kappa|} - 1\right) \tag{14}$$

and

$$\delta = \frac{\alpha^2 Z^2}{n^2}\left(\frac{3}{4} - \frac{n}{|\kappa|}\right). \tag{15}$$

Consequently,

$$E = E_m = -\frac{Z^2}{2n^2(1+\delta)}. \tag{16}$$

By expanding the last equation into a power series with respect to αZ we obtain

$$E = -\frac{Z^2}{2n^2}\left[1 - \frac{\alpha^2 Z^2}{2n^2}\left(\frac{3}{4} - \frac{n}{|\kappa|}\right) + O(Z^4\alpha^4)\right], \tag{17}$$

i.e. the correct Pauli energy.

3. Algebraic representations

Let $\phi_k(r)$, $k = 1, 2, \ldots N$ be a primitive basis set of radial functions which depend upon some nonlinear parameters and let

$$\Phi^{\mathrm{L}}(r) = \sum_{k=1}^{N} C_k^{\mathrm{L}} \phi_k(r) \tag{18}$$

where C_k^{L} are the linear variational parameters. We shall consider two different ways of representing the small component of the radial part of the wavefunction. In the first one, referred to hereafter as the *uncontracted* case

$$\Phi_{\mathrm{u}}^{\mathrm{S}}(r) = \sum_{k=1}^{N} C_k^{\mathrm{S}} \hat{\mathcal{O}} \phi_k(r) \tag{19}$$

where C_k^{S} are variational parameters independent of C_k^{L}. In the second representation, referred to as the *contracted* case,

$$\Phi_{\mathrm{c}}^{\mathrm{S}}(r) = \hat{\mathcal{O}} \Phi_{\mathrm{c}}^{\mathrm{L}}(r). \tag{20}$$

In this case the small component is determined solely by the kinetic balance condition.

In the *uncontracted* case the radial Dirac equation (3) leads to the following algebraic $2N \times 2N$ eigenvalue problem:

$$\boldsymbol{H}(E)\boldsymbol{C} = 0, \tag{21}$$

where

$$\boldsymbol{H}(E) = \begin{pmatrix} \boldsymbol{V} - E\boldsymbol{S} & 2c\boldsymbol{T} \\ 2c\boldsymbol{T} & \boldsymbol{X} - 2(E+2c^2)\boldsymbol{T} \end{pmatrix}, \tag{22}$$

E is the eigenvalue,

$$\boldsymbol{C} = \begin{pmatrix} \boldsymbol{C}^{\mathrm{L}} \\ \boldsymbol{C}^{\mathrm{S}} \end{pmatrix}$$

is the corresponding eigenvector and

$$\begin{aligned} (\boldsymbol{V})_{kk'} &= \langle \phi_k | U | \phi_{k'} \rangle, \\ (\boldsymbol{T})_{kk'} &= \tfrac{1}{2} \langle \phi_k | \hat{\mathcal{O}}^\dagger \hat{\mathcal{O}} | \phi_{k'} \rangle, \\ (\boldsymbol{X})_{kk'} &= \langle \phi_k | \hat{\mathcal{O}}^\dagger \, U \, \hat{\mathcal{O}} | \phi_{k'} \rangle, \\ (\boldsymbol{S})_{kk'} &= \langle \phi_k | \phi_{k'} \rangle. \end{aligned}$$

As it is known [14, 15], the lowest positive energy solutions of equation (21) converge to the bound-state solutions of the corresponding Dirac equations if the primitive basis set approaches completeness. The $2N \times 2N$ matrix $\boldsymbol{H}(E)$ is the representative of the Dirac operator of equation (3) in the large/small component space spanned by $\{\phi_k\}/\{\hat{\mathcal{O}}\phi_k\}$, $k = 1, 2, \ldots, N$ or, alternatively, as a representative of the kinetically balanced Dirac operator of equation (7) in the space spanned by $\{\phi_k\}$. In both cases the result is the same since the spinor and the orbital degrees of freedom are in each of these cases combined differently.

The *contracted* case, by definition, cannot lead to an exact solution of the Dirac equation even in the limit of a complete basis set. Therefore its analysis did not receive much attention in the literature. However it may be very useful as a generator of kinetically-balanced contracted basis sets for relativistic calculations. The algebraic representation of the Dirac equation in the *contracted* case is given by a 2×2 matrix and reads

$$\begin{pmatrix} V_{\mathrm{c}} - ES_{\mathrm{c}} & 2cT_{\mathrm{c}} \\ 2cT_{\mathrm{c}} & X_{\mathrm{c}} - 2(E+2c^2)T_{\mathrm{c}} \end{pmatrix} \begin{pmatrix} C^{\mathrm{L}} \\ C^{\mathrm{S}} \end{pmatrix} = 0, \tag{23}$$

where

$$V_{\mathrm{c}} = \langle \Phi^{\mathrm{L}} | U | \Phi^{\mathrm{L}} \rangle = \sum_{k=1}^{N} \sum_{k'=1}^{N} c_k^* c_k' \langle \phi_k | U | \phi_{k'} \rangle, \tag{24}$$

$$T_{\mathrm{c}} = \tfrac{1}{2} \langle \Phi^{\mathrm{L}} | \hat{\mathcal{O}}^\dagger \, \hat{\mathcal{O}} | \Phi^{\mathrm{L}} \rangle = \tfrac{1}{2} \sum_{k=1}^{N} \sum_{k'=1}^{N} c_k^* c_k' \langle \phi_k | \hat{\mathcal{O}}^\dagger \hat{\mathcal{O}} | \phi_{k'} \rangle, \tag{25}$$

$$X_{\mathrm{c}} = \langle \Phi^{\mathrm{L}} | \hat{\mathcal{O}}^\dagger \, U \, \hat{\mathcal{O}} | \Phi^{\mathrm{L}} \rangle = \sum_{k=1}^{N} \sum_{k'=1}^{N} c_k^* c_k' \langle \phi_k | \hat{\mathcal{O}}^\dagger \, U \, \hat{\mathcal{O}} | \phi_{k'} \rangle, \tag{26}$$

$$S_{\mathrm{c}} = \langle \Phi^{\mathrm{L}} | \Phi^{\mathrm{L}} \rangle = \sum_{k=1}^{N} \sum_{k'=1}^{N} c_k^* c_k' \langle \phi_k | \phi_{k'} \rangle. \tag{27}$$

The linear coefficients c_k and the non-linear parameters in the basis functions may be determined from a variational condition imposed upon the pertinent Rayleigh quotient [17].

The question to be answered is the way one should treat variationally equation (23). One might be tempted to treat it as a 2×2 secular problem and to determine the remaining linear and non-lienar parameters from the energy minimum condition or from a mini-max principle [18, 19]. However, consulting the "exact" kinetically balanced Dirac equation (refdirackb) - (9), we can see that such an approach would imply that we are trying to solve a self-contradictory (???? I have to find in a dictionary the correct English name ????) system of equations. Therefore, with an enlargement of the basis set one may the results to deteriorate rather than to improve (an illustration of this behaviour is given in the next section). Instead we can rearrange equation (23):

$$\frac{1}{m}T_{\rm c} + V_{\rm c} - ES_{\rm c} = 0 \tag{28}$$

$$m + \frac{\alpha^2}{4}\left(\frac{X_{\rm c}}{T_{\rm c}} - 2E\right) - 1 = 0, \tag{29}$$

where m is given by equation (10). The first of these equations is the algebraic representation of equation (8) and the second one – of the condition (9) which determines m. The equations may be solved in the following way. first, by the substitution $\rho = mr$ and by the subsequent application of the Rayleigh-Ritz variational principle one transforms it into the algebraic eigenvalue problem

$$(\boldsymbol{T} + \boldsymbol{V} - E\boldsymbol{S})\,\boldsymbol{c} = 0. \tag{30}$$

The energy E may be minimized also with respect to the nonlinear parameters (an alternative to this procedure may be a minimization of

$$E = (\boldsymbol{T} + \boldsymbol{V})\,\boldsymbol{S}^{-1}$$

simultaneously with respect to all parameters, as it has been done in references [10, 11, 12]. Then the parameter m may be determined from equation (29). The large component of the contracted Dirac basis set function is given by the solution of eqution (30) and the small component by equation (6). The values of $C^{\rm L}$ and $C^{\rm S}$ are determined by equation (10) and by the normalization condition

$$\boldsymbol{S}|C^{\rm L}|^2 + 2\boldsymbol{T}|C^{\rm S}|^2 = 0. \tag{31}$$

A generalization of this procedure to the case of several contracted basis functions is straightforward. An extension to the case of a ϕ-dependent potentials (as it is in the case of Dirac-Fock equations) will be subject of a subsequent publication [20].

4. Examples

In this section we compare the "exact" solutions of equations (7) and the algebraic solutions of equation (23) with the exact Dirac wavefunctions of the $1s_{1/2}$ states of hydrogen-like atoms. The exact Dirac radial wavefunction reads

$$\Phi_{\mathrm{D}}^{\mathrm{exact}} = (2Z)^{\gamma+1/2}(2\Gamma(2\gamma+1))^{-1/2} \begin{pmatrix} (1+\gamma)^{1/2} \\ -(1-\gamma)^{1/2} \end{pmatrix} r^{\gamma} e^{-Zr}, \tag{32}$$

where $\gamma = \sqrt{1-\alpha^2 Z^2}$. The radial part of the "exact" solution of the kinetically-balanced Dirac equation is equal to

$$\Phi_{\mathrm{kb}}^{\mathrm{exact}} = 2(Zm)^{3/2}(4+\alpha^2 Z^2)^{-1/2} \begin{pmatrix} 2 \\ -\alpha Z \end{pmatrix} r e^{-Zmr}, \tag{33}$$

where $m = 1/(1-\alpha^2 Z^2/4)$. The ground-state energy obtained as the solution of the 2×2 secular problem corresponding to equations (7) is equal to

$$E = \langle V_+\rangle - c^2 + \left|\langle V_-\rangle + c^2\right| \sqrt{1 + \frac{2\langle T\rangle}{c^2}\left(1 + \frac{\langle V_-\rangle}{c^2}\right)^{-2}}, \tag{34}$$

where

$$\langle V_\pm\rangle = \frac{1}{2}\left(\frac{V}{S} \pm \frac{X}{2T}\right), \text{ and } \langle T\rangle = \frac{T}{S}. \tag{35}$$

The resulting wavefunction obtained in the Slater-type minimum-basis-set is

$$\Phi_{\mathrm{kb}}^{\mathrm{se}} = (Z\gamma)^{3/2}[(1+\gamma)/2]^{1/2} \begin{pmatrix} 2 \\ -2\alpha Z/(1+\gamma) \end{pmatrix} r e^{-Zr\gamma}. \tag{36}$$

In figure 1 the behaviour of overlap integrals $S_1 = \langle \Phi_{\mathrm{D}}^{\mathrm{exact}} | \Phi_{\mathrm{kb}}^{\mathrm{exact}} \rangle$ and $S_2 = \langle \Phi_{\mathrm{D}}^{\mathrm{exact}} | \Phi_{\mathrm{kb}}^{\mathrm{se}} \rangle$ versus Z is displayed. As one can see, in all cases the wavefunction obtained as a solution of the Schrödinger-type equation gives a better approximation.

In order to check the quality of the wavefunctions constructed as expansion in a Gaussian-type basis, we have selected the large-component basis sets as

$$\phi_k(r)^{\mathrm{GL}} = r^{n_k} \mathrm{e}^{-\mathrm{a_k r^2}}, \qquad , \mathrm{k} = 1, 2, \ldots, \mathrm{N} \tag{37}$$

with $n_k = 1$ and $N = 1, 2, 3, 4, 5$. Then the small-component basis generated by the kinetic balance condition comprises functions

$$\phi_k(r)^{\mathrm{GS}} = r^{n_k+1} \mathrm{e}^{-a_k r^2}, \qquad , k = 1, 2, \ldots, N \tag{38}$$

The energy derived from the 2×2 secular equation is given by equation (34). In the case of the Schrödinger-type equation it is equal to

$$E = \langle T\rangle + \langle V_+\rangle + \langle V_-\rangle. \tag{39}$$

If Ω stands for any of the matrix elements V, T, X, S and $\hat{\Omega}$ — for the corresponding operator, i.e., respectively, for $U(r)$, $\frac{1}{2}\hat{\mathcal{O}}^\dagger\hat{\mathcal{O}}$, $\hat{\mathcal{O}}^\dagger\, U(r)\, \hat{\mathcal{O}}$, I then, in the contracted basis, Ω may be expressed as a combination of two-orbital contributions:

$$\Omega = \sum_{i<j}^{N} R_{ij} \tag{40}$$

Table 1. Expressions defining matrix elements of the algebraic form of the kinetically balanced Dirac equation for the $1s_{1/2}$-type contracted Gaussian basis set. For explanation of symbols see text

Ω	ω_{ij}	$r_1(q)$	$r_2(q)$
V	$-\frac{Z}{2(a_i+a_j)}$	$\frac{4}{1+q}$	$\frac{1}{q}$
T	$\frac{3\sqrt{\pi}\,a_i a_j}{2(a_i+a_j)^{5/2}}$	$\frac{8\sqrt{2}\,q}{(1+q)^{5/2}}$	$\frac{1}{\sqrt{q}}$
X	$-\frac{2Z\,a_i a_j}{(a_i+a_j)^2}$	$\frac{8\,q}{(1+q)^2}$	1
S	$\frac{\sqrt{\pi}}{4(a_i+a_j)^{3/2}}$	$\frac{4\sqrt{2}}{(1+q)^{3/2}}$	$\frac{1}{q^{3/2}}$

where

$$R_{ij} = {c_i}^2 \frac{\omega_{ii}}{N-1} \left[1 + (N-1) f_{ji} r_1(q_{ji}) + f_{ji}^2 r_2(q_{ji}) \right], \qquad (41)$$

$f_{ji} = \frac{c_j}{c_i}$, $q_{ji} = \frac{a_j}{a_i}$, $\omega_{ji} = \langle \phi_j | \hat{\Omega} | \phi_i \rangle$. Explicit expressions for ω_{ji}, and for $r_p(q)$, $q = 1, 2$, may readily be obtained by a direct integration. The resulting formulae, for the basis functions defined in equation (37) with $n_k = 1$ are collected in table 1. Using these equations the energies may be expressed as functions of the parameters defining the basis sets. The energy minimization with respect to these parameters has been performed using the Powell's method [21]. The overlap integrals between the resulting wavefunctions and the exact one are compared in figure 2.

5. Conclusions

We have noticed a possibility of an easy generation of basis sets suitable for relativistic calculations from the nonrelativistic ones. The method consists of the following steps

- Determining $\Phi(\rho)$ by minimizing the Rayleigh quotient resulting from equation (8).
- Determining m using equation (11).
- Rescaling Φ by substitution $\rho = mr$.
- Generation of the small component using equation (6).
- Normalization of the wavefunction using equations (10) and (31)

An extension of this approach to the case of many-electron systems described by Dirack-Fock equations is also feasible and will be subject of a separate publication [20].

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References

[1] Hall G 1950
[2] Roothaan C 1950
[3] Wilson S 199x
[4] review on basis sets 1
[5] review on basis sets 2
[6] Huzinaga et al 198x
[7] Mezey 198x
[8] basis set tabulation 3
[9] Tatewaki - Huzinaga method
[10] Tatewaki H and Koga T 1996 *J. Chem. Phys.* **104** 8493
[11] Tatewaki H, Koga T and Takashima H 1997 *Theor. Chem. Acc.* **96** 243
[12] Koga T, Tatewaki H, Matsuyama H and Satoh Y 1999 *Theor. Chem. Acc.* **102** 105
[13] Malli G and Oreg
[14] Dyall K G, Grant I P and Wilson S 1984 *J. Phys. B: At. Mol. Phys.* **17** L45, 1201
[15] Grant I P 1986 *J. Phys. B: At. Mol. Phys.* **19** 3187
[16] Kutzelnigg W 1984 *Int. J. Quantum Chem.* **25** 107
[17] Tatewaki H *unpublished results*
[18] Talman J D 1986 *Phys. Rev. Lett.* **57** 1091
[19] Kutzelnigg W 1997 *Chem. Phys.* **225** 203
[20] Tatewaki H and Karwowski J *in preparation*
[21] Powell M J D 1964 *Comput. J.* **7** 155.