Vol. B17 (1986) ACTA PHYSICA POLONICA No 9

RATIONALE OF QUASI-RELATIVISTIC METHODS*

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(Received December 20, 1985)

The quasi-relativistic equations of Cowan and Griffin have been derived from the Dirac-Hartree-Fock theory. The one-electron integrals used in both methods are examined and a close relationship between them is established. It is argued that using nonorthogonal orbitals within the quasi-relativistic Hartree-Fock method is correct and in fact necessary.

PACS numbers: 31.10.+z, 31.30.Jv

1. *Introduction*

It is now well established that for both light and heavy systems relativistic effects have to be taken into account in order to bring an overall agreement between theoretical and experimental results [1–9]. Many different methods are currently being used for relativistic calculations of atomic and molecular systems and they account for relativity in one way or another. Of these the variational method based on the Dirac-Coulomb Hamiltonian, i.e. the Dirac-Hartree-Fock (DHF) scheme [10, 11], treats relativistic effects most thoroughly and forms a starting point for a perturbative inclusion of the Breit and quantum-electrodynamic corrections [3, 5–8]. This approach is very suitable for atoms but — due to the variational collapse — fails in the case of analitical calculations for molecules. This is why the methods employing the second-order Dirac equation have recently been developed [12–14]. Perturbative methods on the other hand rely on the Pauli Hamiltonian [15–17] and because of its approximate character can only be used to describe motion of the valence electrons in light systems in which self-consistent effects are small.

The relativistic Hartree-Fock method of Cowan and Griffin (CG) [18, 19], which belongs to the class of quasi-relativistic methods [18–25] falls in between the variational and perturbative schemes. It combines advantages and discards drawbacks of both the DHF and perturbative methods. First of all the CG method operates strictly within the nonrelativistic framework of the Hartree-Fock (HF) method for atoms. As a result the number of radial functions needed to describe an atomic system is significantly reduced.

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* Sponsored, in part, by the Polish Academy of Sciences, project No.MR.I.5.

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Besides the method employs the modified relativistic corrections from the Pauli Hamiltonian in the one-particle equations. This feature allows one to incorporate the relativistic rearrangement of orbitals during the self-consistent-field process. In the CG method the spin-orbit correction is omitted from the quasi-relativistic orbital equation and therefore the total wave function can be written in *LS* coupling instead of *jj* coupling characteristic for the DHF method. This is a very desirable feature of the quasi-relativistic method since most atoms and ions in their ground states are well described by *LS* coupling. Results of various calculations made within the framework of the CG method [18–25] have shown that this method is capable of reproducing the major relativistic effects and yields total energy, orbital and excitation energies, spin-orbit parameters, oscillator strengths, r^{-1} and r^{-2} mean values in good agreement with the DHF results. Recently it has been successfully used to calculate interaction between external fields and atoms [26, 27] and also to calculate total cross-sections and phase shifts in electron and positron scattering by heavy atoms [28]. Also by means of the CG orbitals relativistic effects have been included in molecular calculations [29–32].

Pyykko commenting in his review paper [2] on the use of the quasi-relativistic method wrote: "The theoretical justification of the quasi-relativistic method is not clear but the results must be deemed good". What seems to be most obscure in the quasi-relativistic approach is the very fact that the apparently nonorthogonal quasi-relativistic orbitals are manipulated within the HF scheme which assumes strict orthogonality of orbitals. Also the absence of small components from the self-consistent-field process has so little effect on the quasirelativistic results as compared against the relativistic values. It is rather surprising especially when one notes that the small components of inner orbitals of heavy atoms can hardly be considered small at all. For the 1s orbital of mercury ($Z = 80$), for example, the ratio of radial part of the small component to the large one is 0.32 at the origin and is nearly constant throughout the range. Therefore small components should not be treated as small and their absence in the quasi-relativistic formalism should produce a marked effect. But the above mentioned results of the quasi-relativistic calculations exhibit no sign of such expected deficiencies.

In what follows we will try to clearify these points and give a rationale for the quasi--relativistic Hartree-Fock method. We begin with pointing out approximations necessary to reduce the DHF one-particle equations to the corresponding quasi-relativistic ones. These in turn simplify into the CG equations when the spin-orbit correction is omitted. We further show a close relationship between the one-electron integral in both schemes and give reasons allowing us to interprete the quasi-relativistic expresion for total atomic energy as an approximation to the relativistic DHF one.

2. *Quasi-relativistic Hartree-Fock equations*

Within a single configuration approximation the equations of the DHF method take the form [1]

$$\sigma p \phi_i - 2c[1+(E_i^{\mathrm{DF}} - V^{\mathrm{DF}})/2c^2]\chi_i = \sum_{j \neq i}^{N} E_{ij}\chi_j/c, \tag{1a}$$

$$\boldsymbol{\sigma p}\chi_i-(E_i^{\mathrm{DF}}-V^{\mathrm{DF}})\phi_i/c = -\sum_{j\neq i}^{N} E_{ij}\phi_j/c,$$

$$(i = 1, \ldots, N). \tag{1b}$$

ϕ_i and χ_i are, respectively, the large and small components of the one-particle bispinors ψ_i; $\boldsymbol{\sigma}$ is the vector of the Pauli matrices and E_i^{DF} — the relativistic orbital energy of the i-th electron. The total potential $V^{\mathrm{DF}} = V_{\mathrm{n}}+V_{\mathrm{C}}^{\mathrm{DF}}-V_{\mathrm{x}}^{\mathrm{DF}}$ is the sum of the nuclear $(-Z/r)$, Coulomb and exchange potentials, respectively. Let us evaluate χ_i from Eq. (1a) neglecting nonhomogeneous terms due to the off-diagonal Lagrange multipliers E_{ij} and the nonlocal part of the exchange potential. Thus, approximately, the small component reads

$$\chi_i = B\boldsymbol{\sigma p}\phi_i/2c, \tag{2}$$

where

$$B^{-1} = 1+(E_i^{\mathrm{DF}}-V_{\mathrm{l}}^{\mathrm{DF}})/2c^2$$

with $V_{\mathrm{l}}^{\mathrm{DF}} = V_{\mathrm{n}}+V_{\mathrm{C}}^{\mathrm{DF}}-V_{\mathrm{lx}}^{\mathrm{DF}}$ being a local approximation to the potential V^{DF} [33–36]. Now the small component can readily be eliminated from Eq. (1b). After some manipulations the following 2nd-order integro-differential equations for the large components ϕ_i can be obtained:

$$\{\boldsymbol{p}^2/2+(V_{\mathrm{n}}+V_{\mathrm{C}}^{\mathrm{DF}}-V_{\mathrm{x}}^{\mathrm{DF}})-E_i^{\mathrm{DF}} \tag{3a}$$

$$-(1/c^2)\,(E_i^{\mathrm{DF}}-V_{\mathrm{l}}^{\mathrm{DF}})^2+B(\boldsymbol{p}V_{\mathrm{l}}^{\mathrm{DF}})\boldsymbol{p}-i\boldsymbol{\sigma}B[(\boldsymbol{p}V_{\mathrm{l}}^{\mathrm{DF}})\times\boldsymbol{p}] \tag{3b}$$

$$+(1/c^2)\,(E_i^{\mathrm{DF}}-V_{\mathrm{l}}^{\mathrm{DF}})\,(V_{\mathrm{x}}^{\mathrm{DF}}-V_{\mathrm{lx}}^{\mathrm{DF}})\}\phi_i \tag{3c}$$

$$= \sum_{j\neq i}^{N} E_{ij}^{\mathrm{DF}}\phi_j \tag{3d}$$

$$+(1/2c^2)E_i^{\mathrm{DF}}-V_{\mathrm{l}}^{\mathrm{DF}}\sum_{j\neq i}^{N} E_{ij}^{\mathrm{DF}}\phi_j, \quad (i = 1, \ldots, N). \tag{3e}$$

The left-hand side of the above equations comprises: (*i*) operators familiar from the nonrelativistic HF equations, (3a); (*ii*) the one-particle relativistic corrections, i.s. the mass-velocity, Darwin and spin-orbit terms, respectively, (3b), and (*iii*) the relativistic correction due to nonlocal part of the exchange potential, (3c). The right-hand side sums up contributions due to the orthogonality constraints imposed upon the one-particle wave functions ψ_i. It can be seen that in addition to the term (3d) which has its analog in the HF equations there is also the relativistic correction to the off-diagonal Lagrange multipliers (3e). However the terms (3c) and (3e) may be discarded since thay are of the same order of magnitude as terms which had not appeared in Eq. (3) because of the approximate character of Eq. (2). Note that in the case of configurations leading to zero-diagonal Lagrange multipliers the system of equations (2) and (3) with terms (3c) and (3e) being neglected is exactly equivalent to the equations of the Dirac-Hartree-Fock-Slater method, i.e. the local exchange approximation to the DHF method. In the general case Eqs (2) and (3) are an approximation to the equations of the DHF method. If, in addition, the small components are neglected in Eqs (3) then the following set of the quasi-relativistic Hartree-Fock (QRHF) equations follows:

$$\{\boldsymbol{p}^2/2+(V_\mathrm{n}+V_\mathrm{C}^\mathrm{QR}-V_\mathrm{x}^\mathrm{QR})-E_i^\mathrm{QR}+V_\mathrm{QR}[V_1^\mathrm{QR}]\}\phi_i = \sum_{j\neq i}^{N} E_{ij}^\mathrm{QR}\phi_j, \quad (i = 1, \ldots, N). \tag{4}$$

The two-component functions ϕ_i being their solutions are referred to as the quasi-relativistic wave functions. They can be taken exactly in the form of the Pauli spinors. The small components no longer enter the Coulomb and exchange potentials. This is denoted by superscripts QR added the corresponding symbols. Since the quasi-relativistic potential V_QR contains the spin-orbit term solutions of Eqs (4) are classified by $\boldsymbol{j}^2$ and j_z operators.

Quasi-relativistic wave functions are taken to form both the Coulomb and exchange potentials and so to allow for any practical application of Eqs (4) one has to know how to normalize them. The equations of the DHF method are obtained from the variational principle under assumption that the orbitals are mutually orthogonal and all are normalized to unity. As a result the total energy expression assumes a simple form and the total relativistic wave function is thus normalized in accordance with its statistical interpretation. The above assumptions, however, are not essential and could be relaxed leading to analogous but computationally more complicated scheme. But Eqs (4) for the quasi-relativistic orbitals that approximate the large components of DHF spinors have been derived from the standard DHF equations. So one could argue that the quasi-relativistic orbitals should be normalized accordingly with small components taken into account. But since small components do not appear in the QRHF scheme explicitly the problem of normalization is not at all trivial. Thus to complete the formulation of the QRHF method one has to find out, firstly, how to normalize the quasi-relativistic orbitals and secondly, how to compute the total energy within the QRHF method. As it is shown in the next section the most consequent approach is to take $\langle\phi_i|\phi_i\rangle = 1$. In this case the probabilistic interpretation of a one-particle density is retained and the correct energy expression results.

3. Total energy in QRHF method

Eqs (4) have the form of the nonrelativistic HF equations with the additional local potential V_QR which takes into account the relativistic effects. This potential modifies the nuclear potential V_n. Consequently the one-electron integral in the CG method has been taken in the form [18]:

$$I^\mathrm{QR} = \langle\bar{\phi}^\mathrm{QR}|\boldsymbol{p}^2/2+V_\mathrm{n}+V_\mathrm{QR}[V_1^\mathrm{QR}]\,|\phi^\mathrm{QR}\rangle, \tag{5}$$

where $\bar{\phi}^\mathrm{QR}$ means that $\langle\bar{\phi}^\mathrm{QR}|\bar{\phi}^\mathrm{QR}\rangle = 1$. The two electron integrals have been evaluated as in the nonrelativistic case with the quasi-relativistic orbitals instead of the Hartree-Fock ones. But in order to fulfil the requirements of the HF method, the quasi-relativistic orbitals, used to evaluate total energy according to such modified expression, should be orthogonal and normalized to unity. This is the reason why Barthelat, Pellissier and Durand [22] orthogonalized the quasi-relativistic orbitals before constructing the total potential and evaluating the total energy. But as the derivation leading to Eqs (4) shows, the quasi-relativistic orbitals cannot be orthogonal and their ex post orthogonalization is in fact unjustified. In order to be consistent one should start with the DHF energy expression and apply to it the quasi-relativistic approximation.

The two-electron integrals are functionals of one-particle densities: for the Coulomb integrals exactly and for the exchange ones approximately. As has been shown in [37] the Dirac one-electron density ϱ^D is very well approximated by the corresponding quasi-relativistic density ϱ obtained from a quasi-relativistic wave function normalized to unity. This normalization assures that the part of the small component being proportional to the large one is implicitly taken into account. For the nodeless functions ($1s_{1/2}$, $2p_{3/2}$, $3d_{5/2}$, etc.) the quasi-relativistic density includes nearly the whole contribution due to the small component (in the case of relativistic and quasi-relativistic solutions for the Coulomb potential $-Z/r$ both densities match exactly [38]). As the model calculations for thorium shows [37] in these cases ratio $(\varrho^D-\varrho)/\varrho^D$ is of order 10^{-3} in the entire range. For the other orbitals a greater contribution of their small components are not included when ϱ is evaluated. The ratio is 10^{-2} in the main maximum region of ϱ^D and $(1\text{–}5)\times10^{-1}$ near the origin where the contribution of the small component to the relativistic density is largest. Since the DHF and QRHF orbitals are determined mainly by the one-electron density distribution the relativistic orbital densities are well reproduced by their quasi-relativistic counterparts, i.e. $\varrho^{DF}\approx\varrho^{QR}$. The results gathered in Table I may serve as an indirect illustration of this property. Note that the orbitals ϕ_i approximate the large components of the DHF spinors and in consequence cannot be orthogonal. Thus the density ϱ^{QR} is defined in terms of the nonorthogonal quasi-relativistic orbitals.

TABLE I

Comparison of DHF and QRHF r^{-1} and r^2 mean values for two configurations of U^{+87}

		$1s^2 2s^2 2p_{1/2}$		$1s^2 2s^2 2p_{3/2}$	
		DHF	Δ^a	DHF	Δ^a
$\langle r^{-1}\rangle$	1s	123.39	−0.03	123.44	−0.05
	2s	32.20	−2.18	32.23	−2.19
	2p	32.01	−2.08	23.72	0.03
$\langle r^{2}\rangle$	1s	0.01358	0.0000	0.01358	0.0000
	2s	0.05469	0.0008	0.05464	0.0008
	2p	0.04402	0.0007	0.05340	0.0000

[a] Δ = value (QRHF) − value (DHF).

The one-electron integral of the DHF method is

$$I_i^{\mathrm{DF}} = \langle \psi_i | c\boldsymbol{\alpha}\boldsymbol{p}(\beta - I)c^2 + V_{\mathrm{n}} | \psi_i \rangle, \tag{6}$$

where ψ_i is a bispinor. In principle one can use Eq. (2) and eliminate the small component from Eq. (6). However, it is still needed to ensure a proper normalization of the large component $((\langle \phi | \phi \rangle + \langle \chi / \chi \rangle = 1)$. Eq. (5) has been set on a basis of rather intuitive considerations [18]. Yet it turns out to be a proper quasi-relativistic limit of the DHF expression. Eq. (6). In order to prove this let us start from Eqs (1) which yield the following:

$$\begin{aligned} I_{\psi_i} &= \langle \psi_i | c\boldsymbol{\alpha}\boldsymbol{p} + (\beta - I)c^2 + V_{\mathrm{n}} + V_{\mathrm{Cx}}^{\mathrm{DF}} | \psi_i \rangle \\ &= E_i^{\mathrm{DF}} + \sum_{j \neq i}^{N} E_{ij}^{\mathrm{DF}}(-\langle \phi_i | \phi_j \rangle + \langle \chi_i | \chi_j \rangle) = E_i^{\mathrm{DF}} + L_i^{\mathrm{DF}}, \end{aligned} \tag{7}$$

where $V_{\mathrm{Cx}}^{\mathrm{DF}}$ stands for $V_{\mathrm{C}}^{\mathrm{DF}} - V_{\mathrm{x}}^{\mathrm{DF}}$. Combining the above expression with the definition of I_i^{DF}, Eq. (6), we have

$$I_i^{\mathrm{DF}} = -\langle \psi_i | V_{\mathrm{Cx}}^{\mathrm{DF}} | \psi_i \rangle + E_i^{\mathrm{DF}} + L_i^{\mathrm{DF}}. \tag{8}$$

Similarly Eq. (4) and Eq. (5) lead to

$$I_i^{\mathrm{QR}} = -\langle \tilde{\phi}_i^{\mathrm{QR}} | V_{\mathrm{Cx}}^{\mathrm{QR}} | \tilde{\phi}_i^{\mathrm{QR}} \rangle + E_i^{\mathrm{QR}} + L_i^{\mathrm{QR}}. \tag{9}$$

Now, in order to establish a relationship between I_i^{DF} and I_i^{QR} we have to know the value of $\Delta E_i = E_i^{\mathrm{DF}} - E_i^{\mathrm{QR}} + L_i^{\mathrm{DF}} - L_i^{\mathrm{QR}}$. Comparison of Eq. (4) and Eq. (3) (without the terms 3c and 3e) shows that ΔE_i can be evaluated as

$$\Delta E_i = \langle \tilde{\phi}_i^{\mathrm{QR}} | V_{\mathrm{Cx}}^{\mathrm{DF}} - V_{\mathrm{Cx}}^{\mathrm{QR}} + V_{\mathrm{QR}}[V_1^{\mathrm{DF}}] - V_{\mathrm{QR}}[V_1^{\mathrm{QR}}] \, | \tilde{\phi}_i^{\mathrm{QR}} \rangle \tag{10}$$

by treating the above integrand as a perturbation in Eq. (4). This can be done since $\varrho^{\mathrm{DF}} \approx \varrho^{\mathrm{QR}}$ holds for all the orbitals. Thus combining Eqs (8), (9) and (10) we arrive at the following relationship between the one-electron integrals, namely

$$\begin{aligned} I_i^{\mathrm{DF}} &= I_i^{\mathrm{QR}} - \langle \psi_i | V_{\mathrm{Cx}}^{\mathrm{DF}} | \psi_i \rangle + \langle \tilde{\phi}_i^{\mathrm{QR}} | V_{\mathrm{Cx}}^{\mathrm{DF}} | \tilde{\phi}_i^{\mathrm{QR}} \rangle + \langle \tilde{\phi}_i^{\mathrm{QR}} | \Delta V_{\mathrm{QR}} | \tilde{\phi}_i^{\mathrm{QR}} \rangle \\ &= I_i^{\mathrm{QR}} + \Delta I_{i1} + \Delta I_{i2}, \end{aligned} \tag{11}$$

where $\Delta V_{\mathrm{QR}} = V_{\mathrm{QR}}[V_1^{\mathrm{DF}}] - V_{\mathrm{QR}}[V_1^{\mathrm{QR}}]$, $I_{i1} = -\int V_{\mathrm{Cx}}^{\mathrm{DF}} \Delta \varrho_i d\tau$, $\Delta I_{i2} = \int \Delta V_{\mathrm{QR}} \varrho_i^{\mathrm{QR}} d\tau$ and $\Delta \varrho_i = \varrho_i^{\mathrm{DF}} - \varrho_i^{\mathrm{QR}}$. ΔI_{i1} is in fact the two-electron integral which depends upon $\Delta \varrho$ rather than ϱ^{QR} or ϱ^{DF}. We already know that $\Delta \varrho$ is about 2 orders of magnitude smaller that ϱ^{DF} or ϱ^{QR}. This in turn makes ΔI_{i1} small compared to $\langle \psi_i | V_{\mathrm{Cx}}^{\mathrm{DF}} | \psi_i \rangle$, being itself a small fraction of I_i^{DF}. Moreover, a closer inspection of ΔI_{i2} show that it depends on integrals whose integrands are proportional to either $(E_i^{\mathrm{DF}} - E_i^{\mathrm{QR}})/c^2$ or $(V_1^{\mathrm{DF}} - V_1^{\mathrm{QR}})/c^2$. Thus we conclude that I^{QR} should provide a very good approximation of I^{DF}.

Now, considering the two-electron part of the total energy it is straightforward to show that

$$\langle\psi_i|V_{\mathrm{Cx}}^{\mathrm{DF}}|\psi_i\rangle = \langle\bar{\phi}_i^{\mathrm{QR}}|V_{\mathrm{Cx}}^{\mathrm{QR}}|\bar{\phi}_i^{\mathrm{QR}}\rangle + \langle\psi_i|V_{\mathrm{nlx}}^{\mathrm{DF}}|\psi_i\rangle - \langle\bar{\phi}_i^{\mathrm{QR}}|V_{\mathrm{nlx}}^{\mathrm{QR}}|\bar{\phi}_i^{\mathrm{QR}}\rangle + \int\{V_{\mathrm{Clx}}^{\mathrm{DF}}\Delta\varrho_i + (V_{\mathrm{Clx}}^{\mathrm{DF}} - V_{\mathrm{Clx}}^{\mathrm{QR}})\varrho_i^{\mathrm{QR}}\}d\tau, \tag{12}$$

where $V_{\mathrm{Clx}} = V_{\mathrm{C}} - V_{\mathrm{lx}}$. The difference between the two-electron integrals is due to integrals which depend on either nonlocal part of the exchange potential $V_{\mathrm{nlx}} = V_{\mathrm{lx}} - V_{\mathrm{x}}$ or on $\Delta\varrho$. All these integrals are thus small and so we see that one- and two-electron contributions to the total relativistic energy are well approximated within the QRHF approach. It must be noted again that these considerations apply only under the assumption that ϕ_i^{QR} approximate the large components of the DHF bispinors. Thus ϕ_i^{QR} have to be left nonorthogonal during the self-consistent-field procedure and should be normalized to unity to yield the approximate relativistic orbital densities. This normalization is very desirable since on the one hand it allows one to retain the standard interpretation of a one-particle density and on the other hand it makes the QRHF one-electron integrals to be a good approximation to their DHF counterparts. In order to illustrate approximations involved in the QRHF method the results of the relativistic and quasi-relativistic calculations for $1s^22s^22p_{1/2}$ and $1s^22s^22p_{3/2}$ configurations of U^{+87} have been compared in Table II.

TABLE II

Comparison of DHF and QRHF calculations for two configurations of U^{+87}. $I(nl)$ and $E(nl)$ denote one-electron integrals and orbital energy for nl electron, respectively. Total energy is given together with its one-electron, E_{I}, Coulomb, E_{C}, and exchange, E_{x}, contributions. All values are in atomic units

	$1s^22s^22p_{1/2}$		$1s^22s^22p_{3/2}$	
	DHF	Δ^{a}	DHF	Δ^{a}
$I(1s)$	−4861.04	−1.08	−4861.06	−0.89
$I(2s)$	−1256.61	0.56	−1256.66	0.51
$I(2p)$	−1256.22	0.27	−1088.78	−0.66
$E(1s)$	−4716.18	−4.05	−4722.09	−2.39
$E(2s)$	−1177.61	−1.62	−1179.21	−1.46
$E(2p)$	−1165.84	−3.54	−1013.49	−1.05
E_{I}	−13491.50	−0.76	−13324.22	−1.43
E_{C}	280.17	−7.47	265.11	−4.93
E_{x}	−11.13	0.41	−9.77	1.26
E_{T}	−13222.47	−7.82	−13070.15	−5.09

[a] Δ = value (QRHF) − value (DHF).

4. Conclusions

Starting with the DHF equations we have derived their QRHF analogs which lead to the quasi-relativistic orbitals being the approximate large components of the DHF spinors. It has been shown that although the quasi-relativistic orbitals of the same symmetry are not orthogonal the total energy within the QRHF approach is to be calculated by means of the standard HF expression with (*i*) modified one-electron integrals, (*ii*) without the contributions due to small components but (*iii*) with the quasi-relativistic orbitals normalized to unity.

Although the QRHF method could in principle be used as an alternative of the DHF scheme we do not think it would offer much advantages. It seems quite obvious that the minor numerical simplifications would not outbalance an inevitable loss of accuracy.

The widely used relativistic HF approach of Cowan and Griffin [18, 19] belongs to the class of quasi-relativistic methods. In fact due to the negligence of the spin-orbit term in the quasi-relativistic potential the QRHF method reduces to the CG one. This in turn means that the quasi-relativistic potential is formally allowed to appear in the HF equations provided the orbitals are allowed also to be nonorthogonal. Thus the considerations of the present paper have given the theoretical justification of the CG method. The QRHF method provides the link between the DHF and CG methods and mainly to this reason it has been analysed in this paper.

The author wishes to express his thanks to Professor J. Karwowski for his stimulating discussions and constant encouragement during the course of this work.

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