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A STUDY OF THE HELIUM ISOELECTRONIC SERIES USING RATIONAL TRIAL FUNCTIONS

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The study of the ground state of helium atom using variational functions of the Padé type is extended to the corresponding isoelectronic sequence with $Z = 3$ to $Z = 10$. It is shown that the earlier observation that the nonlinear function of any order is superior to the corresponding linear function, continues to hold good for the entire isoelectronic sequence.

Keywords : Helium-Isoelectronic Series; Rational Trial Functions; Brillouin-Wigner Perturbation

The summation of the Brillouin-Wigner perturbation series subject to the local energy gap approximation had led to a variational function which contains a rational component (Sane *et al.*, 1979*a*). The form of this type of trial function is the same as first studied by Padé (Padé, 1892) in connection with the summation of the formally divergent series. A Padé type variational function is expected on *a priori* considerations to be superior to the usual linear type trial functions. This expectation has been amply confirmed by a detailed study of the ground state of the helium atom (Jolly, 1980; and Jolly *et al.*, 1980*a*, *b*, 1981), where it has been established that a rational trial function achieves a given level of accuracy in the (*i*) expectation values of different operators, (*ii*) quality of the wave function and (*iii*) convergence behaviour, with fewer number of parameters than a linear trial function. We report in this communication an extension of the earlier work to cover the ground states of the eight members ($Z = 3$ to 10) of the helium isoelectronic sequence. The extension has been undertaken with the following objectives. Firstly, it is useful to know whether or not the patterns observed for the helium atom are maintained for the isoelectronic members. Secondly, it is of considerable interest to compare the Z-dependence of the convergence behaviour of rational type and the linear type of trial functions. Finally, an analysis of the functional dependence of the optimized parameters on Z can yield the structural form of the local energy gap which should prove useful in further investigations of this approximation.

METHOD

The hamiltonian for a two-electron atomic system in atomic units ($m_e = e = \hbar = 1$) has the form

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$$H = -\tfrac{1}{2}(\nabla_1^2 + \nabla_2^2) - Z\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}},$$

where Z is the nuclear charge. The ground state wave function for this system can be written as

$$\psi = e^{-zs}\phi(s, t^2, u), \qquad \ldots(1)$$

where z is the effective nuclear charge, ϕ is the correlation factor and the Hylleraas variables s, t, u are

$$s = r_1 + r_2 \quad t = r_1 - r_2 \quad u = r_{12}.$$

The various approximations to ϕ investigated here are categorised below :

1. The separable form $\phi = \phi(u)$ $\ldots(2)$

with
$$\phi_{\text{Padé}}(u) = \phi_{[N,N]}(u) = \frac{\sum_{n=0}^{N} a_n u^n}{\sum_{n=0}^{N} b_n u^n} \qquad \ldots(3)$$

and
$$\phi_{\text{Linear}}(u) = \phi_M(u) = \sum_{m=0}^{M} a_m u^m \qquad \ldots(4)$$

2. The separable form $\phi = \phi(u, t^2) = \chi(u)\,\xi(t^2)$ $\ldots(5)$

with
$$\chi_{\text{Padé}}(u) = \chi_{[N,N]}(u) = \frac{\sum_{n=0}^{N} a_n u^n}{\sum_{n=0}^{N} b_n u^n}, \qquad \ldots(6a)$$

$$\xi_{\text{Padé}}(t^2) = \xi_{[N,N]}(t^2) = \frac{\sum_{n=0}^{N} c_n t^{2n}}{\sum_{n=0}^{N} d_n t^{2n}}, \qquad \ldots(6b)$$

$$\chi_{\text{Linear}}(u) = \chi_M(u) = \sum_{m=0}^{M} a_m u^m \qquad \ldots(7a)$$

and

$$\xi_{\text{Linear}}(t^2) = \xi_M(t^2) = \sum_{m=0}^{M} c_m t^{2m} \qquad \ldots(7b)$$

3. The non-separable form $\phi = \phi(s, t^2, u)$ $\ldots(8)$

with
$$\phi_{\text{Padé}} = \frac{1 + a_1 s + a_2 u + a_3 t^2}{1 + b_1 s + b_2 u + b_3 t^2} \qquad \ldots(9)$$

and $$\phi_{\text{Linear}} = \sum_{n,l,m} c_{nlm} s^n u^l t^{2m} \qquad \ldots(10)$$

The computational procedure for minimization and for calculating the expectation values is the same as discussed in the earlier papers (Jolly *et al.*, 1980*a*, *b*).

Results and Discussion

The energy eigenvalues corresponding to the three categories of trial functions for $Z = 3$ to $Z = 10$ are presented in Tables I, II and III respectively. The observation that the nonlinear function of any order is superior to the corresponding linear function continues to hold good for the entire isoelectronic sequence. For example, the 4-parameter rational function $\phi_{[2,2]}(u)$ matches the accuracy of a 12-parameter linear function $\phi_{12}(u)$ (see Table I) while the function $\chi_{[2,2]}\xi_{[1,1]}$ (Table II) reproduces the best value obtainable with the series function $\chi_7(u)\ \xi_7(t^2)$ to an accuracy of 10^{-4}. Table III shows that the values differ from the exact values only by one part in 10^4. This table also includes the 6-parameter function corresponding to

Table I

Energy expectation values for the helium isoelectronic sequence ($Z = 3$ *to* $Z = 10$) *for some select functions of the type* $\psi = e^{-zs}\phi(u)$

Z	Correlation factor					
	ϕ_2	$\phi_{[1,1]}$	ϕ_4	$\phi_{[2,2]}$	Series limit	Exact
3	7.2683134	7.2683337	7.2684763	7.2684866	7.2684866	7.2799133
4	13.6443849	13.6444279	13.6445760	13.6445888	13.6445888	13.6555650
5	22.0200195	22.0200809	22.0202308	22.0202452	22.0202454	22.0309704
6	32.3954389	32.3955148	32.3956653	32.3956811	32.3956811	32.4062454
7	44.7707366	44.7708239	44.7709745	44.7709910	44.7709913	44.7814439
8	59.1459588	59.1460553	59.1462058	59.1462234	59.1462234	59.1565938
9	75.5211310	75.5212351	75.5213854	75.5214036	75.5214036	75.5317108
10	93.8962683	93.8963787	93.8965288	93.8965474	93.8965475	93.9068024

Table II

Energy expectation values for the helium isoelectronic sequence ($Z = 3$–10) *for some select functions of the type* $\psi = e^{-zs}\chi(u)\ \xi(t^2)$

Z	Correlation factor			
	$\chi_2\xi_2$	$\chi_{[1,1]}\xi_{[1,1]}$	$\chi_4\xi_4$	$\chi_{[2,2]}\xi_{[1,1]}$
3	7.278340	7.278577	7.278794	7.278797
4	13.653941	13.654235	13.654448	13.654465
5	22.029311	22.029644	22.029854	22.029875
6	32.404562	32.404921	32.405129	32.405152
7	44.779742	44.780121	44.780327	44.780357
8	59.154878	59.155272	59.155476	59.155511
9	75.529984	75.530391	75.530593	75.530625
10	93.905069	93.905486	93.905687	93.905725

TABLE III

Energy expectation values for the helium isoelectronic sequence (Z = 3–10) for some select functions of the type $\psi = e^{-zs}\phi(s, t^2, u)$

Z	Correlation factor			Exact
	$(1 + a_1 s + a_2 u + a_3 t^2 + a_4 s^2 + a_5 u^2)$	$\dfrac{1 + a_1 s + a_2 u + a_3 t^2}{1 + b_1 s + b_2 u}$	$\dfrac{1 + a_1 s + a_2 u + a_3 t^2}{1 + b_1 s + b_2 u + b_3 t^2}$	
3	7.279286	7.279823	7.279823	7.279913
4	13.654799	13.655479	13.655492	13.655565
5	22.030114	22.030871	22.030901	22.030970
6	32.405327	32.406109	32.406178	32.406245
7	44.780481	44.781323	44.781362	44.781444
8	59.155597	59.156426	59.156451	59.156594
9	75.530687	75.531567	75.531613	75.531711
10	93.905760	93.906667	93.906714	93.906802

$$\tilde{\phi} = \frac{1 + a_1 s + a_2 u + a_3 t^2}{1 + b_1 s + b_2 u} \qquad \ldots(11)$$

which yields significantly lower energy than given by the Hylleraas 6-parameter function.

The expectation values of other operators have been found to conform to the patterns observed for the helium atom. Similarly, all the members of the sequence show that rational forms are better approximations to the wavefunction and exhibit faster convergence. Since no new feature has emerged from this study, the extensive data are not tabulated.

Additional insight into the convergence behaviour is provided by the following considerations. An Nth order optimized Padé function (3) generates the infinite sequence

$$\phi_{[N,N]}(u) = 1 + A_1^{(N)} u + A_2^{(N)} u^2 + \ldots, \qquad \ldots(12)$$

where the coefficients $A_i^{(N)}$ are determined in terms of the variational parameters $a_i^{(N)}$ and $b_i^{(N)}$. This is evidently a representation of the solution in a higher dimensional subspace than the finite order linear expansions. It is of interest to compare (12) with the finite linear expansion

$$\phi_M(u) = 1 + a_1^{(M)} u + a_2^{(M)} u^2 + \ldots + a_m^{(M)} u^m \qquad \ldots(13)$$

where the $a_i^{(M)}$'s are the optimized parameters. This is done graphically in Figs. 1 and 2. Fig. 1 depicts the variation of the coefficients $A_1^{(N)}(Z)$ and $a_1^{(M)}(Z)$ with the nuclear charge. This emphasizes the fact that the leading u-dependence or the

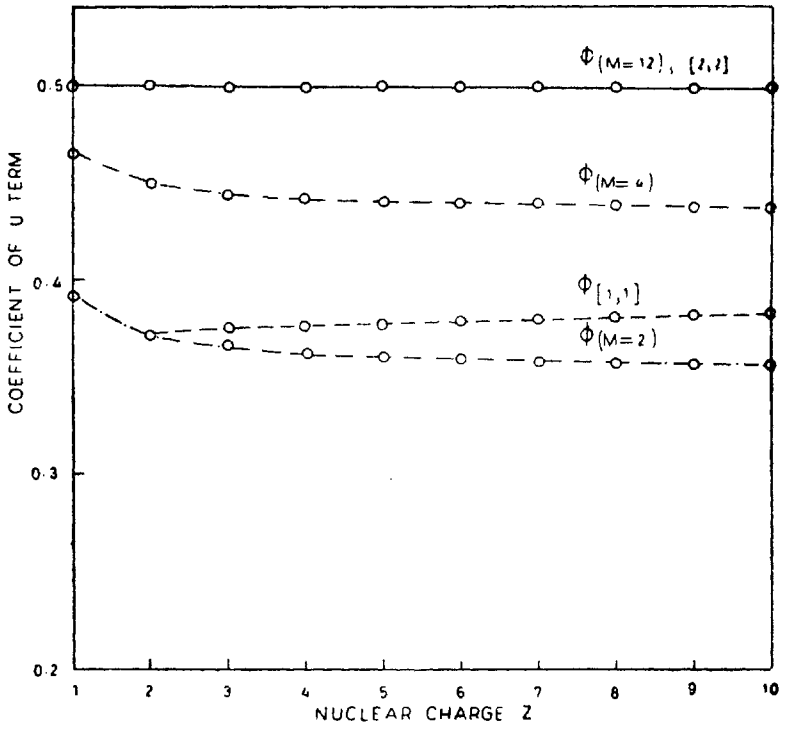

FIG. 1. The variation of the coefficients $A_1^{(N)}(Z)$ and $a^{(m)}_1(Z)$ with the nuclear charge Z for some select functions of the type $\psi = e^{-zs}\phi(u)$.

correlation cusp value (viz., $a_1^{(\alpha)} = 0.5$) is approached much faster by $\phi_{[N,N]}$ than ϕ_M for various orders of approximation. A similar representation of the u^2-dependence is made in Fig. 2 which plots the coefficients $A_2^{(N)}(Z)$ and $a_2^{(M)}(Z)$. The higher order dependence u^r may be similarly analyzed. It is observed that in all cases the coefficient $A_i^{(N)}$ lies closer to the series limit value of the coefficients. This reiterates the ability of the Padé functions to simulate the function $\phi(u)$ with a fewer number of parameters.

We now compare the infinite sequences corresponding to the Padé expansions

$$\chi_{[1,1]}(u) = 1 + A_1 u + A_2 u^2 + \dots . \qquad \dots(14a)$$

and

$$\xi_{[1,1]}(t^2) = 1 + C_1 t^2 + C_2 t^4 + \dots . \qquad \dots(14b)$$

with the truncated linear functions χ_M and ξ_M in Figs. 3, 4 and 5. A comparison of these coefficients against the limiting values for the 'best' function investigated reinforces the earlier conclusions.

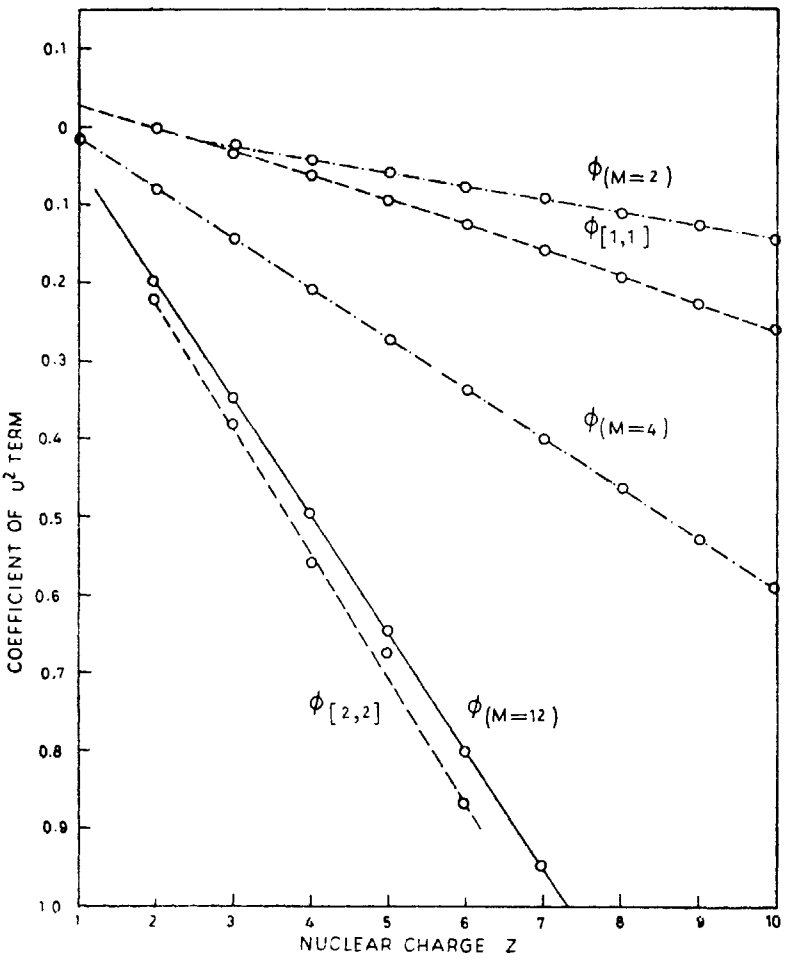

FIG. 2. The variation of the coefficients $A_2^{(N)}(Z)$ and $a_2^{(m)}(Z)$ with the nuclear charge Z for some select functions of the type $\psi = e^{-zs}\phi(u)$.

We turn now to a consideration of the functional dependence of the optimized parameters on the nuclear charge since this has a bearing on the structure of the local energy gap. In view of the preliminary nature of this investigation, attention will be confined to the simplest Padé function, namely, the $\phi_{[1,1]}$ form in the variable u.

It will be recalled that the sum of the Brillouin-Wigner perturbation series under the average energy gap approximation leads to the result

$$\psi = \frac{1}{1 - V/\Delta}\,\phi, \qquad \ldots(15)$$

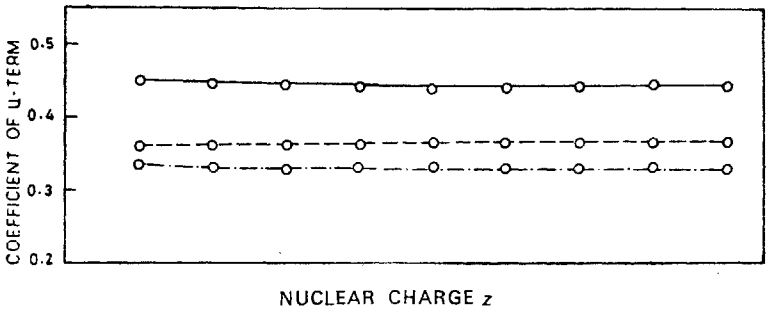

FIG. 3. The variation of the coefficients $A_1^{(N)}(Z)$ and $a_1^{(m)}(Z)$ with the nuclear charge Z for some select functions of the form $\psi = e^{-zs}\chi(u)\,\xi(t^2)$.

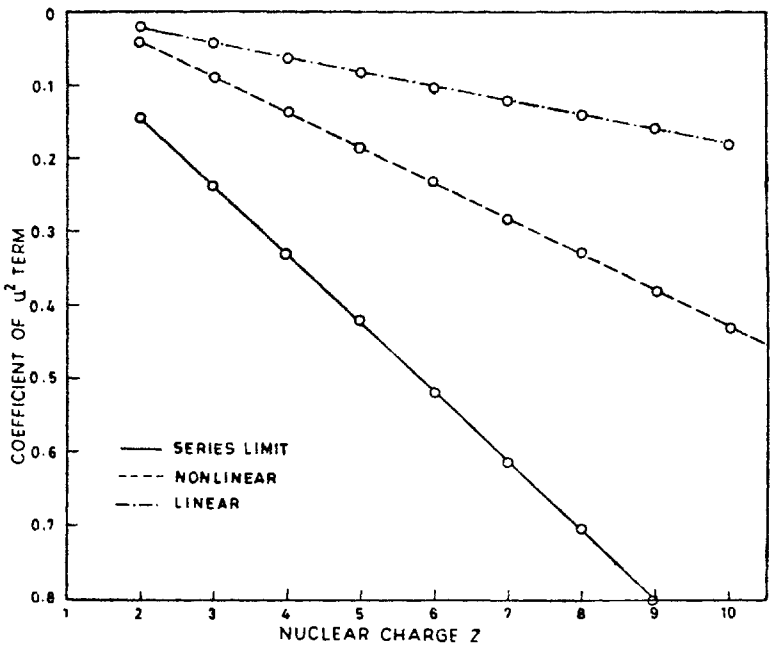

FIG. 4. The variation of the coefficients $A_2^{(N)}(Z)$ and $a_2^{(m)}(Z)$ with the nuclear charge Z for some select functions of the form $\psi = e^{-zs}\chi(u)\,\xi(t^2)$.

where ψ is the approximation for the exact wavefunction, ϕ is the unperturbed wavefunction, Δ (a negative quantity by definition) is the average energy gap and V is the pertubation. Applying eqn. (15) to the helium like atoms $\left(V = \frac{1}{r_{12}}, \Delta = \text{constant}\right)$ leads to a form for ψ which has an incorrect qualitative behaviour and yields very poor energy values (Sane *et al.*, 1979*a*). The next step is to relax the constancy

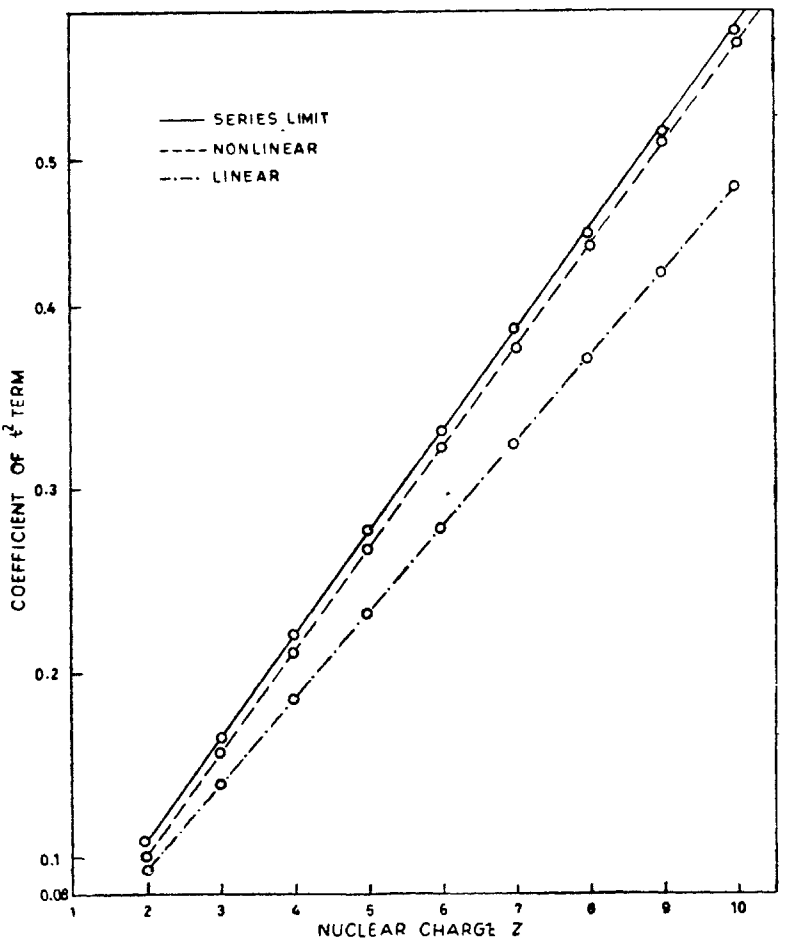

FIG. 5. The variation of the coefficients $C_1^{(N)}(Z)$ and $c_1^{(m)}(Z)$ with the nuclear charge Z for some select functions of the form $\psi = e^{-zs}\chi(u)\,\xi(t^2)$.

requirement on the energy gap and allow it to be a function of the configuration space variables.* It has been shown earlier that if a simple functional relation of the type

$$\Delta = \alpha + \frac{\beta}{r_{12}} \qquad \ldots(16)$$

is assumed, eqn. (15) leads to

$$\psi = \frac{1 + a_1 u}{1 + b_1 u}, \qquad \ldots(17)$$

*The concept of a "local energy" is inadmissible in a strict sense in quantum mechanics. However, situations can arise where the concept proves useful.

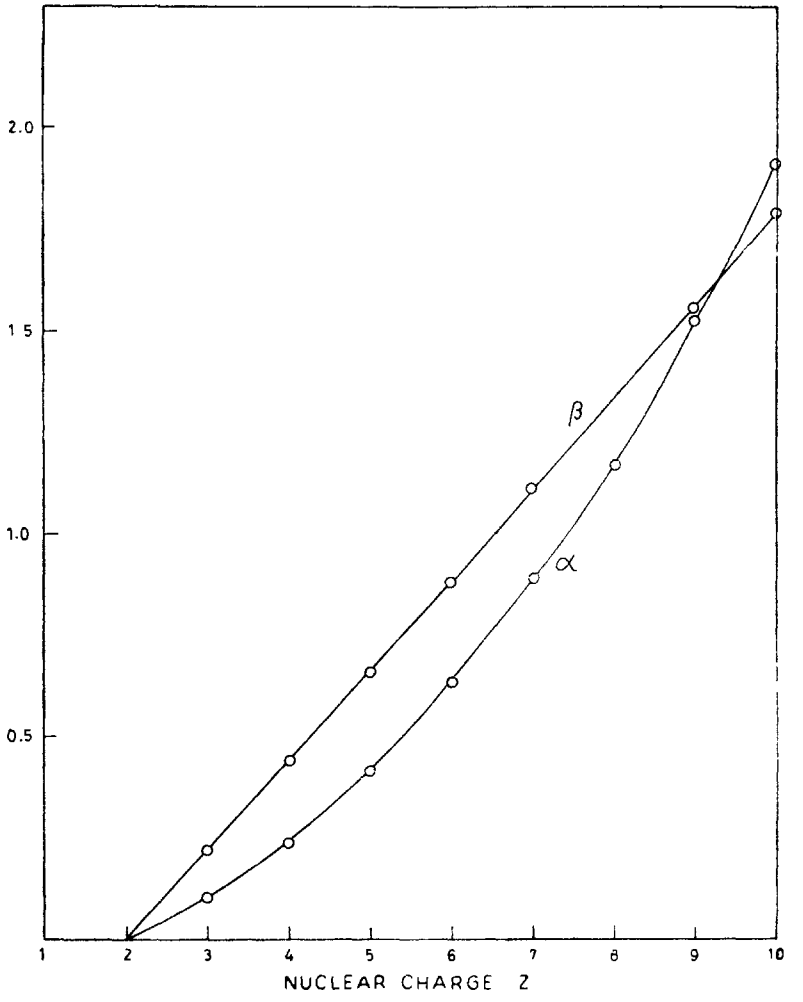

FIG. 6. The variation of the parameters α and β with the nuclear charge Z.

(where $a_1 = \alpha/\beta$ and $b_1 = \alpha/(\beta + 1)$) which belongs to the form given earlier [*see* eqn. (3)]. Thus the [1, 1] Padé form in u is a direct consequence of the local energy gap in eqn. (16). The parameters α and β can be obtained *via* the relations

$$\alpha = \frac{a_1 b_1}{a_1 - b_1} \quad \text{and} \quad \beta = \frac{b_1}{a_1 - b_1} \qquad \ldots(18)$$

Figs. 6 and 7 show that α and β exhibit a quadratic and a linear dependence on Z. The presence of such regularities lends considerable hope that it will be possible to understand in a deeper way, the meaning of the local energy gap approximation.

Finally, we wish to make a remark about the H^--system, which is conspicuous by its absence in our tabulations. As found earlier (Bhattacharjee, 1980; and Sane

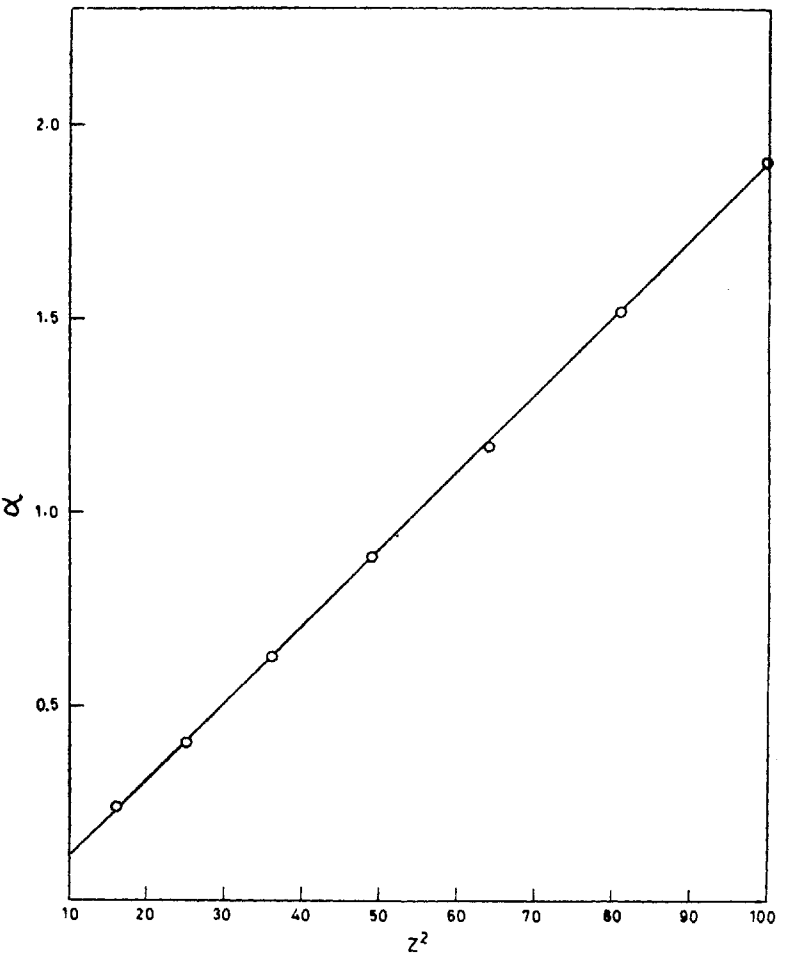

FIG. 7. The variation of the parameter α with Z^2.

et al., 1979*b*), the superiority of the Padé type functions is expected to be most noticeable for the H^--system, i.e., the system containing the strongest pertubation in the isoelectronic sequence. Unfortunately, H^- ion has proved to be as Hylleraas has so aptly described it, the "enfant terrible". For this system the lower order Padé forms have their poles in the physical region, indicating thereby the necessity of using the higher order approximations. The method for proceeding in such circumstances has been discussed in another communication (Jolly *et al.*, 1981). However, the present computational facilities available to us are inadequate. A comprehensive study of the higher order forms will be considerably facilitated if optimization programmes are developed which recognise the special requirements of Padé type trial functions, such as the presence of poles and the very low convergence in the vicinity of a minimum and the necessity of an efficient search for a minium after one local minimum

has been found. When such facilities become accessible, H^--system will become amenable to study.

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