of the nature of the substituent (R). The band can be tentatively assigned to the ring-breathing mode. A characteristic, strong or of medium intensity band at ~670 can be assigned to the ring deformation mode rather than for some fundamental modes of the other groups.

The spectra of the compounds in aqueous media show regular changes with pH of the medium, especially the CT band. The absorbance of the CT band decreases with increases in pH, meanwhile a new band develops at a shorter wavelength. Both the bands overlap to a large extent giving a very broad absorption band. At pH ⩽ 8 the original band vanishes and the new band only is observed. The spectra show a clear isosbestic point indicating the existence of an equilibrium between the non-charged molecules and ionized species. These equilibria correspond to proton elimination from the enol form. The plot of absorbance as a function of pH gives typical dissociation or association curve. These results are utilized for the determination of pKa of the compounds employing (i) the half-height method[6], (ii) the modified limiting absorbance method[7], and (iii) the colleter methods as modified for acid-base equilibria[4]. The mean pK_a values obtained are given in Table 1.

The position and extinction of the different absorption bands of the investigated compounds, are influenced by the nature of substituents. The observed λ_{max} changes in a more or less regular manner with the electron donor-acceptor character of the substituent (R). This fact finds support in the approximate linear correlation between λ_{max} and σ (the Hammett constant). Both λ_{max} and ϵ_{max} of the absorption bands seem to be readily influenced by the nature of the solvent used. The application of the Gati and Szalay[9] equation reveals that the shift in band position is not essentially due to changes of the dielectric constant of the medium. Also, the dielectric functions given by Suppan[10] are not valid

supporting that the role played by the dielectric constant of the medium is not the main factor responsible for the shift observed. The shift of the bands would thus be due to combined effect of several factors essentially the dielectric properties of the solvent and the specific solute-solvent interaction.

It is observed that $\nu C=O$ (cyclic) shifts to lower frequency with increse in the value of Hammett's σ constant of substituent (R). Also, the plot of νNH versus σ (Hammett constant) is more or less linear. The relatively somewhat low values of the νNH may arise from possible intramolecular association through hydrogen bonding. Resonance through the molecule influences the bond order of $C=N$ and $N=N$ groups, consequently the frequency values of the two groups change in the same way.

The plot of pKa as function of σ-constant is almost a linear relation, indicating the dependence of pKa on the nature of the substituent. The values increase as the donor property of the substituent increases.

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TABLE 1 — DISSOCIATION CONSTANTS OF THE COMPOUNDS IN AQUEOUS SOLUTIONS

[λ_{max} in nm, ϵ_{max} in litre mol^{-1} cm^{-1} × 10^{-3}]

Compd.	Nonionic		Ionic		pKa*			
	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}	(i)	(ii)	(iii)	Mean
I$_a$	425	7.3	380	3.4	7.85	7.60	7.95	7.8
I$_b$	440	8.2	385	7.6	8.40	8.40	8.45	8.4
I$_c$	456	6.5	390	3.2	8.70	8.70	8.90	8.8
I$_d$	430	—	390	—	5.40	5.30	5.50	5.4
I$_e$	420	9.7	370	8.4	6.50	6.20	6.20	6.3
I$_f$	430	—	390	—	6.85	6.70	6.85	6.8
I$_g$	450	—	360	—	6.60	6.55	6.65	6.6
I$_h$	436	7.6	384	5.6	8.35	8.35	8.45	8.4
I$_i$	452	2.1	384	7.4	8.50	8.40	8.65	8.5
I$_j$	430	—	390	—	6.80	6.80	6.80	6.8
I$_k$	415	10.2	380	8.1	6.20	6.25	6.45	6.3
I$_l$	425	—	384	—	6.15	6.10	6.05	6.1

*(i) Half-height method[6]
(ii) Limiting absorbance method[7].
(iii) Colleter method[8].

A Study of [1,1] Padé Type Variational Function for Hydrogen as a Test System

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A [1,1] Padé type variational function is shown to be superior to a linear variational function with the same number of parameters for 'strong perturbation' in the ground state of the hydrogen atom treated as a test system. Although considerably poorer than the [2,2] function studied earlier, the [1,1] function is nevertheless found to be sufficiently accurate to be useful—especially in view of its comparative simplicity—for such applications where high precision is not required.

THE summation[1] of the infinite order Brillouin-Wigner perturbation series subject of the "local energy gap" approximation has suggested the use of Padé type functions as trial functions for solving the Schrödinger equation by the variational method. Such functions have been employed so far with remarkable success on the hydrogen-like atoms treated[2] as a test system and on the ground state of the helium atom[3]. In the earlier study of the ground

state of the hydrogen atom[2], a [2,2] Padé type trial function containing four variational parameters was shown to be almost as good as the exact function. However, there can arise situations where such a high precision is not required. For such cases, the less accurate [1,1] form may be adequate. The chief advantage of the [1,1] form is that since it contains only one nonlinear parameter, integrations and energy optimization involving it are less cumbersome than for the [2,2] form which has two non-linear parameters. The aim of the present investigation is to assess the utility of the [1,1] Padé type variational function for the ground state of the hydrogen atom[4].

The Hamiltonian H of a hydrogenic atom with nuclear charge $Z+1$ is written in atomic units as

$$H = H_0 + V \qquad \dots (1)$$

$$\text{where } H_0 = -\tfrac{1}{2} \nabla^2 - \frac{Z}{r} \qquad \dots (2)$$

$$\text{and } V = -\frac{1}{r} \qquad \dots (3)$$

Approximation to the ground state wavefunction of Eq. (1) can be obtained by employing for the trial function, Ψ_{trial} the following form,

$$\Psi_{trial} = \frac{1 + a_1 r}{1 + b_1 r} e^{-Zr} \qquad \dots (4)$$

The pre-exponential factor in Eq. (4) can be recognized as a [1,1] Padé type function in the variable r. For reasons discussed earlier[2], the exponent Z is not treated as a variational parameter. The accuracy of Eq. (4) is judged by comparing it with the exact ground state function of Eq. (1) as well as with the linear variational function with different number of parameters. The method of evaluation of the integrals $<\Psi \mid H \mid \Psi>$ and $<\Psi \mid \Psi>$ for the non-linear and the linear trial functions is the same as described earlier[2].

Table 1 lists the results obtained for energy and the moments ($<r^n>$) for $Z=1$ to 3 for the exact, the [1,1] Padé type, and the linear variational wavefunctions. The $Z=1$ case — the case involving the strongest perturbation — is in many ways the most interesting. The calculated value for the two-parameter Padé type function in this case differs from the exact value by 0.005 a.u., i.e. by only 0.25%. Accuracy of a similar order is achieved by a linear variational function with four paramters. The agreement for $<r>$ and $<r^2>$ is within 5% but it progressively worsens for the higher moments. The first few linear

TABLE 1 — COMPARISON OF ENERGY AND MOMENTS FOR THE EXACT, THE NON-LINEAR AND THE LINEAR WAVE FUNCTIONS FOR Z=1 to 3

[All numbers are in atomic units $(m = e = \hbar = 1)$]

Wave function	No. of parameters	Energy	$<r>$	$<r^2>$	$<r^3>$	$<r^4>$	$<r^5>$	$<r^6>$
			For the case $Z = 1$					
Exact	0	—2.000	0.750	0.750	0.937	1.406	2.461	4.921
Non-linear	2	—1.995	0.768	0.794	1.055	1.863	4.834	19.005
Linear	1	—1.833	1.000	1.500	3.750	15.000	78.750	472.50
Do	2	—1.957	0.814	1.002	2.478	12.410	85.268	653.31
Do	3	—1.991	0.760	0.820	1.577	7.176	55.508	509.28
Do	4	—1.998	0.750	0.767	1.139	3.552	25.762	267.05
Do	5	—2.000	0.750	0.754	0.990	2.044	10.489	109.55
Do	6	—2.000	0.750	0.751	0.949	1.570	4.809	39.754
Do	7	—2.000	0.750	0.750	0.940	1.444	3.071	15.075
			For the case $Z = 2$					
Exact	0	—4.500	0.500	0.333	0.277	0.277	0.324	0.432
Non-linear	2	—4.499	0.501	0.334	0.276	0.271	0.308	0.399
Linear	1	—4.430	0.527	0.366	0.332	0.424	0.813	2.169
Do	2	—4.494	0.500	0.334	0.292	0.348	0.616	1.605
Do	3	—4.500	0.500	0.333	0.280	0.291	0.380	0.691
Do	4	—4.500	0.500	0.333	0.278	0.279	0.332	0.475
Do	5	—4.500	0.500	0.333	0.278	0.278	0.325	0.438
Do	6	—4.500	0.500	0.333	0.278	0.278	0.324	0.433
Do	7	—4.500	0.500	0.333	0.278	0.278	0.324	0.432
			For the case $Z = 3$					
Exact	0	—8.000	0.375	0.187	0.117	0.088	0.077	0.077
Non-linear	2	—7.999	0.375	0.187	0.116	0.086	0.074	0.072
Linear	1	—7.964	0.378	0.185	0.112	0.081	0.073	0.089
Do	2	—7.998	0.374	0.187	0.118	0.091	0.087	0.104
Do	3	—8.000	0.375	0.187	0.117	0.088	0.077	0.078
Do	4	—8.000	0.375	0.187	0.117	0.088	0.077	0.077
Do	5	—8.000	0.375	0.187	0.117	0.088	0.077	0.077
Do	6	—8.000	0.375	0.187	0.117	0.088	0.077	0.077
Do	7	—8.000	0.375	0.187	0.117	0.088	0.077	0.077

functions are, however, even worse in this respect and it takes about seven variational parameters before the linear function becomes comparable to the Padé function.

The superiority of the non-linear form over the linear form decreases rapidly as Z is increased (Table 1). This feature has been observed for the [2,2] function also. It is understandable because as the 'perturbation' becomes weaker, the distinction between the [1,1] form (which represents an infinite series) and a polynomial expansion progressively disappears.

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Initiating Free Radical in the Aqueous & Emulsion Polymerization of Vinyl Monomers, Initiated by the Ferric/Bisulphite or Ferric/Metabisulphite Redox Systems

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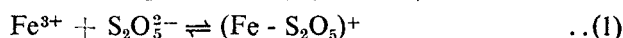
Potassium metabisulphite ($K_2S_2O_5$) when added to a ferric chloride solution, gives an orange red colour which persists for a long time at 0°C, but vanishes almost immediately at room temperature (30 to 35°C). The orange red solution initiates vinyl polymerisation under nitrogen atmosphere almost instantaneously, but the colourless solution fails to do so. It is proposed that the orange red colour is due to the formation of a complex, (Fe-HSO$_3$)$^{2+}$ or (Fe-S$_2$O$_5$)$^+$, which produces $\dot{S}O_3^-$ ion radicals by the redox reaction, and these initiate vinyl polymerization in aqueous media. It is observed that the pH of the FeCl$_3$ solution decreases when $K_2S_2O_5$ is added to it. Initiation of polymerization of methyl methacrylate, methyl acrylate, acrylonitrile, acrylamide, etc. by the Fe^{3+}-S$_2$O$_5^{2-}$ system is almost instantaneous under nitrogen atmosphere, whereas initiation by S$_2$O$_5^{2-}$ alone is a very slow process under identical experimental conditions if the monomer is methyl methacrylate or ethyl methacrylate.
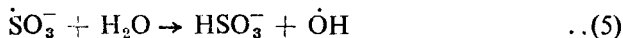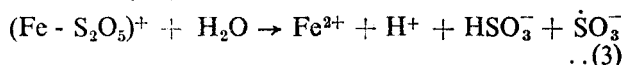
IT is well known that ferric bisulphite ions act as potential redox initiators[1,2] of vinyl monomers in aqueous or emulsion polymerization. However, very little is known about the redox reaction itself. In this note, we report some observations made in the Fe^{3+} - S$_2$O$_5^{2-}$ reaction.

It has been observed that when potassium metabisulphite ($K_2S_2O_5$) is added to a ferric chloride solution, an orange red colour is produced, the stability of which is a function of temperature. At 0°C,

the colour persists for a long time, whereas at room temperature (30 to 35°C) it vanishes almost instantaneously, as soon as it is formed on mixing the reagents. If a mixture of FeCl$_3$ and $K_2S_2O_5$ is made in stoichiometric proportion at 0°C under nitrogen atmosphere, then the solution is capable of initiating vinyl polymerization as long as the orange red colour persists. The colourless solution does not initiate vinyl polymerization. No polymerization however occurs in the presence of free radical scavengers, viz. hydroquinone. The pH of the salt solutions at two temperatures (0° & 30°C) have been measured (Table 1), and it is found that the pH of the media decreases when FeCl$_3$ reacts with bisulphite or metabisulphite. It is known that $K_2S_2O_5$ when added to water, gives bisulphite[3], (HSO_3^-), and the orange red colour appears to be due to the formation of a complex between Fe^{3+} ions and HSO_3^- or $S_2O_5^{2-}$ ions, (Eqs. I & 2)

$$Fe^{3+} + S_2O_5^{2-} \rightleftharpoons (Fe\text{-}S_2O_5)^+ \qquad ..(1)$$

$$Fe^{3+} + HSO_3^- \rightleftharpoons (Fe\text{-}HSO_3)^{2+} \qquad ..(2)$$

The complexes generate free radicals possibly via reactions (3-5).

$$(Fe\text{-}S_2O_5)^+ + H_2O \rightarrow Fe^{2+} + H^+ + HSO_3^- + \dot{S}O_3^- \qquad ..(3)$$

$$(Fe\text{-}HSO_3)^{2+} \rightarrow Fe^{2+} + H^+ + \dot{S}O_3^- \qquad ..(4)$$

$$\dot{S}O_3^- + H_2O \rightarrow HSO_3^- + \dot{O}H \qquad ..(5)$$

Reactions (3) and (4) will account for the decrease in pH of the media, while (3), (4) and (5) will account for the initiation of vinyl polymerization and for the nonhydrolysable sulphonate and also hydroxyl end groups of the polymers[4,5]. The initiating free radicals are therefore $\dot{S}O_3^-$ and $\dot{O}H$, but not HSO_3, SO_3H (in the absence of added H$^+$ ions), or $\dot{S}O_3^-$, as postulated by others[2,5,6]. Fitch et al[5]. suggested that the redox reaction could be represented by equation (6)

$$Fe^{3+} + HSO_3^- \rightarrow Fe^{2+} + \dot{S}O_3H \qquad ..(6)$$
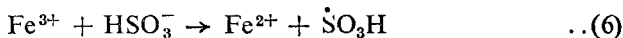
However, these authors did not elaborate the nature of the free radical. HSO_3^- ion is known to have

TABLE 1 — pH OF SALT SOLUTIONS MEASURED AT 0° AND 30°C

Solution (aqueous)	pH	
	30°	0°C
0.05% FeCl$_3$	2.50	2.70
0.05% K$_2$S$_2$O$_5$	4.90	5.45
0.05% FeCl$_3$ + ⎫	2.30	2.70
0.05% K$_2$S$_2$O$_5$ ⎭	(colourless solution)	(orange red colour solution) & 2.50 (colourless solution)

Note : The pH meter (M/s Systronics Ltd, Calcutta) was calibrated with a series of buffer solutions at two temperatures (0° & 30°C) as given by Willard et al[7].