Correlated wave functions for three-body systems with Coulomb interaction. Mesonic molecular ions

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The previously reported general correlated wave function for three-particle Coulomb systems is analyzed term by term for the cases of H^-, $e^-e^+e^-$, $p\mu p$, $d\mu d$, $t\mu t$, and $p\mu d$ to find how sensitive the single terms are to the configuration of the Coulomb systems, and how effective they are in giving accurate results. It is found that on going from one-center Coulomb systems to systems with increasing two-center configuration, the leading terms in the wave function become those containing powers of the relative distance between the particles with the same sign of the charges. For mesonic molecular ions, a two-term wave function has been found to give highly accurate ground-state energy results: -2776.87 eV for $p\mu p$, -2982.97 eV for $d\mu d$, -3069.15 eV for $t\mu t$, and -2867.77 eV for $p\mu d$. All of the wave-function parameters are tabulated together with a number of useful expectation values.

I. INTRODUCTION

A number of relatively recent developments in atomic theory have renewed interest in explicitly correlated wave functions for three-body systems with Coulomb interaction. Three of such developments have been mentioned in a recent paper by Winkler and Porter[1]; namely, (1) the work done by Bopp,[2] where is shown that the energies of ground and excited states of N-electron atoms are given to a very good approximation in zeroth order by a sum of energies of appropriate states of two-electron atoms; (2) the calculations of the autoionizing states of He and H^- with correlated wave functions[3,4]; and (3) the calculations of long-range atomic interaction potentials of two He-like atoms by using one-electron densities.[5]

We may still quote the quite recently reported measurements of the differential cross sections of the $(e, 2e)$ reaction in He,[6] which is considered an important probe in the investigation of He correlated wave functions, the Hartree-Fock wave function having been ruled out by experiment.[7] We can also quote a recent analysis of the binding limits in two-electron atoms, which has demonstrated the inapplicability of the independent-electron viewpoint and the necessity of using correlated wave functions.[8]

In general, correlated wave functions are known to be of crucial importance in the calculation of several atomic and molecular properties[9] and in obtaining meaningful results in many collision problems.[10] Detailed investigations of this subject concerning several two-electron systems have been performed recently by Banyard and co-workers.[11-15]

Correlated wave functions are mostly formulated by means of the configuration-interaction (CI) method or by the use of correlation factors which explicitly contain the interparticle coordinates x_{ij}. Although electron correlation calculations for molecules and large atoms are usually based on the CI method, excellent results may be also obtained for relatively complex atoms and molecules with wave functions explicitly containing factors depending on x_{ij}.[16]

With this in mind, in a previous paper,[17] henceforth referred to as I, we proposed for three-body systems with Coulomb interaction the general explicitly correlated wave function

$$\Psi^{(n)}(x_1x_2x_3) = \sum_{i=1} A_i \Phi_i(x_1x_2x_3), \tag{1}$$

where

$$\Phi_i(x_1x_2x_3) = F_i(\alpha_i, \beta_i) G_i(i-1, \gamma_i), \tag{2}$$

with F an open-shell wave function,

$$F(\alpha, \beta) = e^{-\alpha x_1 - \beta x_2} + e^{-\beta x_1 - \alpha x_2} = f(\alpha, \beta) + f(\beta, \alpha), \tag{3}$$

and G a correlation function,

$$G(p, \gamma) = x_3^p e^{-\gamma x_3}. \tag{4}$$

A similar general correlated wave function has been recently proposed by Somorjai and Power,[18,19] in connection with the work of Somorjai and coworkers on the integral-transform method. The previous work along similar lines is found in Refs. 2–8 of I.

In I the wave function $\Psi^{(n)}$ has been applied in its three "orders" $\Psi^{(1)}$, $\Psi^{(2)}$, and $\Psi^{(3)}$ to H^-, $e^-e^+e^-$, and $p\mu p$ as test systems. All of the ob-

tained results compared very favorably with the most accurate calculations. However, the results for $p\mu p$ were slightly inferior in accuracy to those for H^- and $e^-e^+e^-$. Clearly, the same analytical function does not give results of identical accuracy when applied to one-center and two-center three-body systems.

It is the main purpose of this paper to analyze term by term the first terms Φ_i of the general expansion $\Psi^{(n)}$ for a number of three-body systems of rather different configurations to find out which are the most effective terms for each of them. Secondly, we wish to construct for mesonic ions wave functions as accurate as those for H^- and $e^-e^+e^-$ reported in I.

II. ANALYSIS OF THE WAVE FUNCTION

To find the most effective terms Φ_i for a given three-body Coulomb system, we calculate variationally the ground-state energies,

$$E_i = \langle \Phi_i | H | \Phi_i \rangle / \langle \Phi_i | \Phi_i \rangle , \tag{5}$$

and a number of other simple expectation values (see Sec. III) of H^-, $e^-e^+e^-$, $p\mu p$, $d\mu d$, $t\mu t$, and $p\mu d$ for successive Φ_i. H entering in (5) is the Hamiltonian of an arbitrary three-body Coulomb system, which is given in I in interparticle coordinates x_1, x_2, and x_3, together with other details. As to the analytical forms of Φ_i, what really changes in successive Φ_i is the power p in the correlation function (4). In general, each Φ_i contains three variational parameters, α_i, β_i and γ_i, to be optimized.

Next, to construct accurate wave functions we take the linear combination

$$\Psi_{ij}(x_1x_2x_3) = \Phi_i^{B}(x_1x_2x_3) + c\Phi_j^{NB}(x_1x_2x_3) , \tag{6}$$

Φ_i^{B} and Φ_j^{NB} being, respectively, the "best" and the "next-best" single-term wave functions. The ansatz (6) implicitly states that the best energy with a two-term wave function is expected to be obtained by combining the best and next-best single-term functions Φ_i and Φ_j, and reoptimizing all parameters entering into Ψ_{ij}. This statement must be understood not as having general validity, but simply as a result of an analysis of the different pairs (Φ_i, Φ_j) partly reported in Table II. Although the analysis is far from being complete, the conclusion concerning our specific wave functions may realistically be considered as definitive. In a single-term variational calculation, such as that reported in Table I, if the parameter p were allowed to be free, almost certainly the best energy E would occur for noninteger p values (as partially evidenced by Schröder[20]). Since in our calculation p is not allowed to be nonintegral, the best combination Ψ_{ij} is then that containing the single terms Φ_i and Φ_j, with the parameters p_i and p_j the closest to the "true" p. Such single-term wave functions are clearly those we termed best and next best. On the other hand, the trend of all other pairs Ψ_{ij} may be predicted only very approximately.

TABLE I. Term-by-term analysis of the general wave function $\Psi^{(n)} = \sum_{i=1}^{n} A_i \Phi_i$. E_i is the energy obtained with the wave function $\Phi_i = F_i(\alpha_i, \beta_i) G_i(i-1, \gamma_i)$. $i-1=p$ is the power of x_3 in the correlation function G, $m = (m_1 + m_2)/2m_3$ and m_i $(i=1,2,3)$ being the particle masses. The energies are in a.u. for H^- and $e^-e^+e^-$, and in mesonic a.u. for the mesonic molecular ions.

	$i-1$	$-E_i$	m [a]
H^-	0	0.513 303	0
	1	0.511 875	
	2	0.498 552	
	3	0.496 390	
$e^-e^+e^-$	0	0.256 652	1
	1	0.259 395	
	2	0.253 464	
	3	0.247 151	
$p\mu p$	0	0.461 349 [b]	8.88
	1	0.486 735	
	2	0.491 266	
	3	0.490 436	
	4	0.487 558	
$d\mu d$	0	0.485 928 [b]	17.75
	1	0.517 312	
	2	0.525 658	
	3	0.528 099	
	4	0.527 989	
	5	0.526 609	
	6	0.524 545	
$t\mu t$	0	0.494 694 [b]	26.58
	1	0.528 505	
	2	0.538 504	
	3	0.542 428	
	4	0.543 660	
	5	0.543 499	
	6	0.542 549	
$p\mu d$	0	0.473 335 [b]	13.31
	1	0.471 771	
	2	0.478 832	
	3	0.479 699	
	4	0.477 761	

[a] The mass values (in units of the electron mass) for the muon, proton, deuteron, and triton are 206.77, 1836.12, 3670.4, and 5496.8, respectively.

[b] A mesonic a.u. of energy is $m_\mu e^4/\hbar^2 = 5626.21$ eV.

The results of the calculations are shown in Tables I–III. From Table I, where the results of the term-by-term analysis of the general expansion (1) are shown, it can be seen that the best and the next-best wave functions are

TABLE II. Two-term analysis of the general wave function $\Psi^{(n)}$. E_{ij} is the energy obtained with the wave function $\Psi_{ij}=\Phi_i+c\Phi_j$. $i-1=p_i$ and $j-1=p_j$ are the powers of x_3 in the correlation functions G_i and G_j. The energies are defined as in Table I.

	$(i-1,j-1)$	$-E_{ij}$
$e^-e^+e^-$	0,1	0.261 501
	0,2	0.260 950
	1,2	0.260 332
	1,3	0.260 034
	0,3	0.257 471
	2,3	0.256 090
$p\mu p$	2,3	0.493 511
	1,3	0.493 384
	1,4	0.493 129
	1,2	0.492 442
	2,4	0.492 217
	0,3	0.492 170
	0,2	0.491 929
	3,4	0.491 724
	0,4	0.491 205
	0,1	0.487 004

H^-: Φ_1, Φ_2, $p=0,1$,

$e^-e\ e^-$: Φ_2, Φ_1, $p=1,0$,

$p\mu p$: Φ_3, Φ_4, $p=2,3$,

$d\mu d$: Φ_4, Φ_5, $p=3,4$,

$t\mu t$: Φ_5, Φ_6, $p=4,5$,

$p\mu d$: Φ_4, Φ_3, $p=3,2$.

If m_1 and m_2 are the masses of the particles with the same sign of the charge, and m_3 the mass of the binding particle, it results that the values of p in $G(p,\gamma)$ [Eq. (4)] giving the best single-term wave function increase regularly with the increase of the quantity

$$m=(m_1+m_2)/2m_3.$$

Looking at Table I it may remarked that for symmetric mesonic molecular ions simple single-term wave functions give surprisingly good results. For the asymmetric system $p\mu d$ the results are less satisfactory, but it must be recalled that because of the absence of symmetry, for $p\mu d$ we use only the first part, $f(\alpha,\beta)=e^{-\alpha x_1-\beta x_2}$, of the open-shell wave function $F(\alpha,\beta)$. Hence the resulting wave functions for $p\mu d$ are analytically simpler than the corresponding ones for the symmetric mesonic systems.

Table II displays the energy results calculated for all possible Ψ_{ij}, combining and reoptimizing the single-term wave functions reported in Table I (for $e^-e^+e^-$ and $p\mu p$ only).

Table III reports the energies and the variational parameters corresponding to the best single-term and $\Psi_{ij}(x_1x_2x_3)$ wave functions for the mesonic molecular ions. The data concerning H^- and $e^-e^+e^-$ are not reported here, because they confirm the results previously reported in I, and in this sense are not new. In fact, for H^- the best single-term wave function Φ_1 coincides with $\Psi^{(1)}$, while for both H^- and $e^-e^+e^-$ the $\Psi_{ij}(x_1x_2x_3)$ wave function coincides with $\Psi^{(2)}$ (for $e^-e^+e^-$ the best single-term wave function Φ_2 does not coincide with $\Psi^{(1)}$).

Again, it must be remarked that the two-term wave functions Ψ_{ij} give accurate energy results, in spite of their simple and compact form. In particular, for $p\mu p$ the two-term Ψ_{ij} is found to be better than the three-term function $\Psi^{(3)}$. In general, the energy results compare very favorably with the most accurate calculations (see Table V below).

To save computer time, in this analysis we have confined ourselves to the optimization of only the two-term wave function (6), Ψ_{ij}; it is clear, however, that further improvement may be obtained with the next approximation, e.g., with the three-term configuration

$$\Psi_{ijk}=\Phi_i^B+c\Phi_j^{\mathrm{NB}}+d\Phi_k^{\mathrm{TB}}, \tag{7}$$

Φ_k^{TB} being the third-best single-term wave function, as found in Table I. That this is the case can be inferred from the results reported in I, where for both H^- and $e^-e^+e^-$ the wave functions $\Psi^{(2)}$ and $\Psi^{(3)}$ coincide with the present Ψ_{ij} and Ψ_{ijk}, respectively. In going from $\Psi^{(2)}$ to $\Psi^{(3)}$ the ground-state energy passes from $-0.261\,501$ to $-0.261\,721$ a.u. for $e^-e^+e^-$, and from $-0.527\,221$ to $-0.527\,363$ a.u. for H^-. Hence it is legitimate to expect a similar improvement also for the mesonic molecular ions. However, the ansatz (7) indicates only a way to proceed. It does not exclude the possibility that even better three-term wave functions may be constructed by adding to Ψ_{ij} single-term wave functions Φ_k other than Φ_k^{TB}. For $p\mu d$, Ψ_{ij} is found to improve drastically the poor results obtained with the single-term wave functions Φ_i; however, the results are still inferior to those for symmetric mesonic ions (see Table V). This is an indication that the general wave function (1), in order to be used with greater success for asymmetric mesonic ions, needs some modifications, or the approximations such as $\Psi^{(1)}$, $\Psi^{(2)}$, $\Psi^{(3)}$ or Φ_i, Ψ_{ij}, and Ψ_{ijk} must be built up in a somewhat different way. This is why in the present work we have confined ourselves to $p\mu d$ only.

III. EXPECTATION VALUES AND FINAL COMMENTS

As is customary, we have calculated, together with the ground-state energies, a number of simple expectation values useful in applications and

TABLE III. Data for mesonic molecular ions. p_i and p_j are the powers of x_3, while α_i, β_i, γ_i, c, α_j, β_j, and γ_j are the variational parameters of the trial functions Φ_i and $\Psi_{ij}=\Phi_i^B+c\Phi_j^{NB}$. N is the normalization constant. $(\partial E/\partial q)_W$ and $(\partial E/\partial q)_b$ are the worst and the best values of the energy derivatives with respect to the variational parameters. E is the ground-state energy. $\Delta=(E/E_b)\times 100\%$ is a percentage value, E_b being the best available in the literature value. E_{vt} is a quantity derived from the virial theorem condition, which should be equal to E in an exact calculation. All quantities are in mesonic a.u.

	$p\mu p$		$d\mu d$		$t\mu t$		$p\mu d$	
	Φ_3	Ψ_{34}	Φ_4	Ψ_{45}	Φ_5	Ψ_{56}	Φ_4	Ψ_{43}
p_i	2	2	3	3	4	4	3	2
p_j		3		4		5		3
α_i	0.960 886	1.280 649	0.211 701	0.300 475	0.212 686	0.296 128	0.517 250	0.156 186
β_i	0.206 733	0.282 781	1.025 602	1.348 654	1.051 634	1.325 021	0.702 599	1.027 360
γ_i	0.813 287	1.394 811	1.327 965	2.007 642	1.814 520	2.525 210	1.306 078	0.910 852
c		0.231 441		0.238 391		0.186 845		0.919 606
α_j		0.896 413		0.184 725		0.182 312		0.955 619
β_j		0.180 886		0.957 723		0.976 738		0.266 052
γ_j		1.029 664		1.562 799		2.015 303		1.184 687
$10\times N$	0.408 100	0.783 466	0.776 058	1.587 722	1.182 097	2.672 515	1.684 395	0.551 858
$(\partial E/\partial q)_w$	1.93×10^{-7} [a]	5.43×10^{-5} [f]	1.95×10^{-7} [a]	8.07×10^{-5} [e]	1.68×10^{-7} [a]	-1.27×10^{-4} [b]	2.40×10^{-7} [c]	4.36×10^{-7} [e]
$(\partial E/\partial q)_b$	-1.17×10^{-7} [b]	2.24×10^{-6} [a]	-1.39×10^{-7} [b]	9.71×10^{-6} [g]	-3.09×10^{-8} [b]	4.46×10^{-6} [d]	5.37×10^{-8} [a]	3.43×10^{-7} [g]
$-E$	0.491 266	0.493 559	0.528 099	0.530 191	0.543 660	0.545 510	0.479 699	0.509 717
$-E_{vt}$	0.491 266	0.493 511	0.528 099	0.530 093	0.543 660	0.545 267	0.479 699	0.509 719
$\Delta(\%)$ [h]	99.33	99.79	99.46	99.85	99.55	99.89	93.57	99.43

[a] $q=\alpha_1$.
[b] $q=\beta_1$.
[c] $q=\gamma_1$.
[d] $q=A$.
[e] $q=\alpha_2$.
[f] $q=\beta_2$.
[g] $q=\gamma_2$.
[h] In mesonic a.u., $-E_b(p\mu p)=0.494\,578$ (Ref. 24); $-E_b(d\mu d)=0.530\,966$ (Ref. 23); $-E_b(t\mu t)=0.546\,105$ (Ref. 23); $-E_b(p\mu d)=0.512\,662$ (Ref. 23).

TABLE IV. $\langle x_j^n \rangle$ are the expectation values of some powers of the interparticle distances ($n = 1, 2, -1$; $j = 1, 2, 3$). d is the relative rms displacement, χ the diamagnetic susceptibility, and γ_a ($a = p, d, t$) the muon-nucleus overlaps. All quantities are in mesonic a.u.

	$p\mu p$		$d\mu d$		$t\mu t$		$p\mu d$	
	Φ_3	Ψ_{34}	Φ_4	Ψ_{45}	Φ_5	Ψ_{56}	Φ_4	Ψ_{43}
$\langle x_1 \rangle$ [a]	2.3962	2.3978	2.1283	2.1353	2.0214	2.0335	2.2483	2.4394
$\langle x_2 \rangle$	2.3962	2.3978	2.1283	2.1353	2.0214	2.0335	1.8559	2.1051
$\langle x_3 \rangle$	3.3341	3.3118	2.8604	2.8522	2.6668	2.6708	2.7051	3.1176
$\langle x_1^2 \rangle$	7.8126	7.8296	5.9774	6.0433	5.3092	5.4140	6.1947	7.9255
$\langle x_2^2 \rangle$	7.8126	7.8296	5.9774	6.0433	5.3092	5.4140	4.3667	5.9649
$\langle x_3^2 \rangle$	12.6896	12.4772	9.0785	9.0242	7.7494	7.8014	8.0666	10.9600
$\langle x_1^{-1} \rangle$	0.6656	0.6690	0.7243	0.7272	0.7495	0.7519	0.6046	0.6390
$\langle x_2^{-1} \rangle$	0.6656	0.6690	0.7243	0.7272	0.7495	0.7519	0.7669	0.7471
$\langle x_3^{-1} \rangle$	0.3487	0.3509	0.3923	0.3942	0.4117	0.4134	0.4121	0.3667
d	0.3762	0.3709	0.3310	0.3307	0.2994	0.3061	0.3199	0.3572
$10^6 \times \chi$	11.6152	11.6404	8.8866	8.9847	7.8933	8.0491	7.8510	10.3255
γ_p	0.5505	0.5805					0.2280×10^{-2}	0.4847
γ_d			0.5738	0.6017			0.4669×10^{-2}	0.6335
γ_t					0.5858	0.6110		

[a] A mesonic a.u. of length is $a_\mu = \hbar^2/m_\mu e^2 = 2.559\,22 \times 10^{-11}$ cm.

in assessing the accuracy of the wave functions. In particular, for $p\mu p$, $d\mu d$, $t\mu t$, and $p\mu d$ we have calculated the following:

(a) The expectation values of some powers of the interparticle distances $\langle x_j^n \rangle$ ($n = 1, 2, -1$; $j = 1, 2, 3$).

(b) The relative rms displacement

$$d = [(\langle x_3^2 \rangle - \langle x_3 \rangle^2)/\langle x_3 \rangle^2]^{1/2},$$

which is a measure of the diffuseness of the wave function.

(c) The diamagnetic susceptibility, which for any atomic system is given by[21]

$$\chi = 0.743\,36 \times 10^{-6} \sum_{i=1}^{2} \langle x_i^2 \rangle.$$

(d) The quantity

$$E_{vt} = \tfrac{1}{2}(\langle x_3^{-1} \rangle - \langle x_1^{-1} \rangle - \langle x_2^{-1} \rangle),$$

coming directly from the virial theorem condition

$$\langle V \rangle = -2\langle T \rangle,$$

V and T being the potential and the kinetic energy operators of the three-Coulomb-particle Hamiltonian appearing in (5). In an exact calculation $-E_{vt}$ should be equal to the ground-state energy. The deviation $z = E - E_{vt}$ is a measure of the accuracy of minimization of the trial wave function.

(e) The muon-nucleus overlap γ_N, of importance in the analysis of the muon capture experiments. γ_N is defined as the ratio of the muon density at the nucleus N in the molecular ion $N\mu N'$ (averaged over the separation between the nuclei N and N') to the muon density at the nucleus N in the $N\mu$ atom[22-24]:

$$\gamma_N = \frac{\langle \Psi | \delta(\vec{\mathbf{x}}_{\mu N}) | \Psi \rangle}{\langle \phi_N | \delta(\vec{\mathbf{x}}_{\mu N}) | \phi_N \rangle} = \frac{4\pi}{|\phi_N(0)|^2} \int_0^\infty |\Psi(0, x_3, x_3)|^2 x_3^2 \, dx_3. \tag{8}$$

In (8) N stands for p, d, and t, $\vec{\mathbf{x}}_{\mu N}$ is the vector radius of the muon with respect to the nucleus N and in Ψ substitutes for $\vec{\mathbf{x}}_1$ or $\vec{\mathbf{x}}_2$. $\phi_N(\vec{\mathbf{x}}_{\mu N})$ is the ground-state normalized wave function of the $N\mu$ mesonic atom. Ψ is now normalized.

(f) The percentage values

$$\Delta = (E/E_b) \times 100\%,$$

E_b being the best available (in the literature) energy value of the Coulomb system with which we are concerned. Δ is a measure of accuracy of our energy results.

(g) The best and the worst values of the energy derivatives with respect to the variational parameters, $(\partial E/\partial q)_b$ and $(\partial E/\partial q)_w$. These quantities, which must be zero in an exact variational calculation, are a measure of the degree of the minimization of a given trial wave function, and complement E_{vt}.

(h) The normalization constant N.

The results concerning the quantities discussed under points (d), (g), and (h) are reported in Table III, while all of the others are found in Tables IV and V, where they are compared with the per-

TABLE V. Comparisons with data available from the literature.

	$\langle x_3 \rangle$	d	γ_p	γ_d	γ_t	$-E$	Reference
$p\mu p$	3.3118	0.3709	0.580 506			2776.87	This work
	3.3077		0.5733			2782.20 [a]	24
	3.3037					2748.44	26
	3.3651	0.3879				2769.78	17
	3.291	0.3585				2765.50	20
	2.8913	0.3155				2761.27 [a]	28
			0.654			2769.26 [a]	27,22
			0.568			2781.44	23
						2777.60 [a]	29
$d\mu d$	2.8522	0.3307		0.601 768		2982.97	This work
				0.585		2987.35	23
	2.838 29					2978.77	26
	2.855	0.3278				2971.74	20
	2.652 25	0.2985				2971.44 [a]	28
						2984.12 [a]	27
						2980.57 [a]	29
$t\mu t$	2.6708	0.3061			0.611 049	3069.15	This work
	2.655 254					3069.57	26
					0.595	3072.50	23
	2.666	0.2997				3058.81	20
$p\mu d$	3.1176	0.3572	0.4847	0.6334		2867.77	This work
	3.081 97					2858.21	26
			0.507	0.641		2884.33	23
	3.100	0.3462				2867.22	20
	2.790 22	0.3056				2859.35 [a]	28
						2876.19 [a]	27

[a] Values corrected with respect to the original to be consistent with $m_\mu = 206.77$.

tinent literature.

The reported comparisons show that our simple and compact correlated wave functions give accurate results not only for the energy, but also for other expectation values. This is true, in particular, also for muon-nucleus overlaps γ_N, which are not geometrical in nature and hence not strictly related to the energy of the system, as is the case for the mean distances.

In general, relatively simple combinations of terms of the wave function $\Psi^{(n)}$ have proved quite effective in giving accurate results for three-body Coulomb systems of very different configurations. With a two-term wave function we have obtained energy values quite close to the best values available in the literature, obtained, as a rule, by means of very lengthy polynomial expansions (see Table V).

In particular we have obtained the following energy results (in parentheses is Δ, the percentage value with respect to the best literature value): -2776.87 eV (99.72%) for $p\mu p$; -2982.97 eV (99.85%) for $d\mu d$; -3069.15 eV (99.89%) for $t\mu t$; and -2867.77 eV (99.43%) for $p\mu d$.

We have not tested the wave functions $\Psi^{(n)}$ on the He and He-like atoms, nor on H_2^+. However, from the results of I for H^-, and from Bonham and Kohl's results for He and Li^+,[25] it is easy to infer that relatively simple correlated wave functions of type $\Psi^{(n)}$ will work for these atoms as well as they have worked for H^-. This seems to be true also for H_2^+ and similar molecular ions, as is seen from Schröder's work[20] and some of our preliminary calculations. The results for $p\mu d$ appear to be slightly less accurate; in particular, the muon overlaps calculated with the single-term wave function Φ_4 are clearly very poor (see Table IV). On the contrary, Ψ_{43} shows a drastic improvement over the Φ_4 results, and gives accurate expectation values (see Table V). Further improvement is provided by the combination

$$\Psi_{435} = \Phi_4 + c\Phi_3 + d\Phi_5,$$

which gives for the energy $E = -2871.08$ eV (99.54%).

In conclusion, we believe that also for the asymmetric mesonic molecular ions and other Coulomb systems not considered here, it is possible to construct simple combinations of terms Φ_i to give highly accurate results.

A computer program based on the Klessing-Polak conjugate gradient algorithm has been worked out to minimize the energy expression (5), and it was run on the IBM 370/145 of the University of Palermo Computation Center. The optimization of a single-term wave function took, on the average, about 2 min of cpu time, while about 20 min were required for two-term wave functions.

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