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Exchange- and Correlation-Energy Calculations in Finite Systems*

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In the local-effective-potential approximation of the Kohn-Sham self-consistent scheme applied to an atomic system, it was reported that while the calculated exchange energies for various atoms were accurate to within 10%, the correlation energies of atoms were too large by a factor of 2. A model system is set up to study the reason why the exchange energy estimates are so much better than those of the correlation energy even though they were treated on the same footing. It was found that, in using expressions derived from an infinite electron gas system to study finite systems, the major source of error comes from the fact that the low-lying levels of a finite system are discrete and have finite spacings. The replacement of summation by integration in the perturbation diagrams results in an overestimate of correlation energy, and a small error in the exchange energy in a finite system like an atom.

INTRODUCTION

In an earlier paper[1] (hereafter referred to as I) the Kohn-Sham self-consistent scheme was applied to study atomic systems. The local-effective-potential approximation was used. In this approximation, the defined exchange- and correlation-energy functional $E_{xc}[n]$ (for definitions of various terms, see the review article by Kohn[2]) was approximated as

$$E_{xc}[n]=\int \epsilon_{xc}(n(\vec{r}))\,n(\vec{r})\,d\vec{r}\ , \tag{1}$$

where $\epsilon_{xc}(n)$ is the single-particle exchange and correlation energy of an infinite homogeneous interacting electron gas of density n equal to the local density of the system at $\vec{r}$.[3]

The exchange and the correlation energies of atoms were estimated in a way described in detail in I. It was reported that while the calculated exchange energies for various atoms were accurate to within 10%, the correlation energies of atoms were too large by a factor of 2. The accuracy for both quantities improves for larger atoms. These statements were illustrated by the numbers listed in Tables II and III of I. Kelly[4] and Lundqvist and Ufford[5] also observed that correlation energies of atoms calculated by using the Gell-Mann and Brueckner[6] formula for a homogeneous electron gas is too large by a factor of approximately 2 for small atoms.

It is the purpose here to look for the reason why the exchange-energy estimates are so much better than those of the correlation energy in the calculation in I, even though they were treated on the same footing. The result illuminates the applicability of such general methods as using the knowledge obtained from an infinite homogeneous electron gas to study finite electron systems like atoms. In a way it also clarifies and answers some of the comments made by various authors[7,8] on such methods. These will be discussed in Sec. III.

A major difference between an infinite electron gas system and a finite system is that one has a continuous energy spectrum and the other has discrete levels. In an infinite system, the excited states form a continuum above the ground state. The system is therefore "soft," i.e., the electrons have low-lying levels available to adjust themselves to some disturbance, as for example, their mutual Coulomb repulsion. The correlation energy, which is a measure of how well the electrons manage to avoid each other, is high. On the other hand, in finite systems like atoms, the excited states have a discrete spectrum. Virtual excitations of the electrons, to avoid their Coulomb repulsion, involve finite energy increments. Thus these systems are "harder," and their actual correlation energies per electron are smaller.

That this effect can be quite substantial can be seen as follows. To the second-order perturbation theory, the correlation energy diverges logarithmically near zero excitation energy. Thus to this order, the low-lying states contribute overwhelmingly. Even when higher-order corrections are introduced, which make the correlation energy finite, low-lying intermediate states still contribute a large share of the total correlation energy. In atoms these low-lying states are missing. In Eq. (1), we used for ϵ_{xc} an expression obtained from studies of an infinite homogeneous interacting electron gas. Hence it is not altogether surprising that our calculated correlation energy exceeds the actual correlation energies by as much as a factor of 2.

The exchange energy, on the other hand, is a first-order correction and does not involve virtual excitations. The discreteness of energy levels does not affect it as much.

To give a more quantitative foundation to these arguments, we shall study a model system with a finite number of electrons in a finite "periodic" box. In Sec. I the model is defined and explained. The exchange and correlation energies of this model system are analyzed in Sec. II. Further discussion will be given in Sec. III. In order to give a more fluent presentation, side discussions and details are put in Appendices A and B.

I. MODEL SYSTEM

Consider a cubic box containing an interacting homogeneous electron gas of a finite number N. Let the electron density in the box attain that of an average atom. Such densities n correspond roughly to r_s less than 0.3, where $r_s \equiv (3/4\pi n)^{1/3}$. We shall examine the local-effective-potential approximation when it is applied to this system.

In the high-density regime, the Gell-Mann–Brueckner method[6] of evaluating the correlation energy by summing up the most divergent ring diagrams [Fig. 1(a)] is valid. We shall, therefore, concentrate on such ring diagrams. In order to see the effect of finite N, we shall examine the contribution of the second-order ring diagram in which the interaction is replaced by a screened Coulomb potential

$$V(\alpha, r) = (-e^2/r)\exp(-\alpha r) \ , \tag{2}$$

where α is the screening constant. The choice of α is discussed in Appendix A. For electron densities corresponding to those found in atoms, the relevant value of α is approximately 0.2. α is always measured in units of k_F, the "averaged" Fermi momentum defined by

$$(k_F/2\pi)^3 = 3N/8\pi\Omega \ , \tag{3}$$

where N is the total number of electrons in the box of volume Ω. We shall study two cases: $\alpha = 0.18$ and $\alpha = 0.25$. The conclusions do not differ by much.

The use of a screening constant is roughly equivalent to the inclusion of all the polarization parts. In a way, it substitutes for all the higher-order ring diagrams summed by Gell-Mann and Brueckner (Appendix A; see also Pines, Ref. 9).

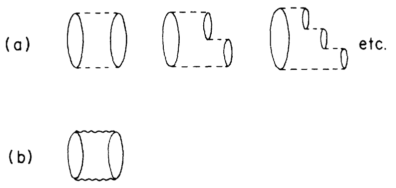

FIG. 1. Ring diagrams. The dashed line is the Coulomb interaction $V(r) = -1/r$. The wavy line is the screened Coulomb interaction $V(r) = -e^{-\alpha r}/r$.

We shall explicitly evaluate the second-order ring diagram with a screened interaction (a) for the model system of finite N, and (b) for an infinite homogeneous gas system at the same density. The results are compared.

The exchange energies can be evaluated for both systems without the introduction of screening.

II. CORRELATION AND EXCHANGE ENERGY

The second-order ring diagram contribution to the correlation energy of the model system is

$$\epsilon_{\text{corr}}(\alpha, N) = \frac{1}{2N\hbar^2} \sum_{\text{spin}} \sum_{k_i, k_j \le k_F} \sum_{k_m, k_n \ge k_F} \frac{2M}{k_i^2 + k_j^2 - k_m^2 - k_n^2} \times |\langle k_m k_n | V(\alpha) | k_i k_j \rangle|^2 \ . \tag{4}$$

Here $V(\alpha)$ is given by expression (2), and k_F is defined as in Eq. (3). M is the mass of an electron.

In the evaluation of the summations both the Pauli principle and the conservation of momentum $\vec{k}_i + \vec{k}_j = \vec{k}_m + \vec{k}_n$ must be satisfied. If we let $\Omega = a^3$, and express energy in rydbergs, this becomes

$$\epsilon_{\text{corr}}(\alpha, N) = -\frac{1}{4N\pi^4} \sum_{\text{spin}} \sum_{k_i, k_j \le k_F} \sum_{k_m, (\vec{k}_i + \vec{k}_j - \vec{k}_m) \ge k_F} \frac{1}{[(\vec{k}_m - \vec{k}_i)^2 + (\vec{k}_m - \vec{k}_i)\cdot(\vec{k}_i - \vec{k}_j)]} \frac{1}{[(\vec{k}_m - \vec{k}_i)^2 + \alpha^2]^2} \ , \tag{5}$$

where α is the screening constant. For $N \le 114$, the summation can be carried out term by term (Appendix B). In the case of $N = 162$, the Monte Carlo method was used.

In the limit of an infinite system $N \to \infty$, at density n we can replace the summation by an integration using the rule

$$\sum_{\vec{k}} \to \frac{\Omega}{(2\pi)^3} \int d^3\vec{k} \ . \tag{6}$$

The integration has been carried out by Huby[10] with the result

$$\epsilon_{\text{Huby}}(\alpha) = \lim_{N\to\infty} \epsilon_{\text{corr}}(\alpha, N)$$

$$= -\frac{2}{\pi^2} \Big([\tfrac{13}{16} - \ln 2 + \tfrac{3}{16}(\tfrac{1}{2}\alpha)^2] \ln[1 + (2/\alpha)^2] - \tfrac{7}{24} + \tfrac{49}{24}\ln 2 + \tfrac{5}{8}\ln 2\,(\tfrac{1}{2}\alpha)^2 + \tfrac{3}{4}\cot^{-1}(2/\alpha)\,[(2/\alpha) - \tfrac{1}{3}\alpha]$$

$$+\tfrac{3}{4}\left[(1/\alpha)+\tfrac{1}{2}\alpha+\tfrac{1}{2}(\tfrac{1}{2}\alpha)^3\right]\int_0^{\tan^{-1}(2/\alpha)}\ln(2\cos\chi)\,d\chi+\tfrac{1}{2}\left[3+(\tfrac{1}{2}\alpha)^2\right]\int_0^1\frac{\ln(1-\chi^2)}{\chi^2+(2/\alpha)^2}\,d\chi$$

$$-2(2/\alpha)^2\int_0^1\frac{\tanh^{-1}\chi\,d\chi}{\chi[\chi^2+(2/\alpha)^2]}\Bigg)\ . \qquad (7)$$

The integrals left in the above expression can be evaluated numerically for the chosen α.

The final results are stated in Table I. The values of ϵ_{corr} for our model systems are characterized by the number N. The last row gives the infinite homogeneous case ϵ_{Huby} at the same density. The ratio $\psi_c(N)\equiv\epsilon_{\text{corr}}(N)/\epsilon_{\text{Huby}}$ is also shown. We see at once that as N increases, $\epsilon_{\text{corr}}(N)$ approaches ϵ_{Huby} very slowly. In a moderately large system ($N\sim 54$), $\psi_c(N)$ is around 0.6. This may be compared with the ratios of the actual correlation energies in atoms to those calculated from our infinite gas model, which are in the vicinity of 0.5 (cf. Tables II and III of I).

The exchange energy of a homogeneous electron gas is

$$\epsilon_x(N)=-\frac{1}{2N}\frac{4\pi e^2}{\Omega}\sum_{\text{spin}}\sum_{k_i,k_j<k_F}\frac{1}{(\vec{k}_i-\vec{k}_j)^2}\ . \qquad (8)$$

We can write the above as

$$\epsilon_x(N)=\epsilon_x(\infty)\psi_x(N)\ , \qquad (9)$$

where

$$\epsilon_x(\infty)=-0.916/r_s\ , \qquad (10)$$

$$\psi_x(N)=\frac{16k_F^2}{9N}\sum_{k_i,k_j<k_F}\frac{1}{(\vec{k}_i-\vec{k}_j)^2}\ , \qquad (11)$$

and $k_F r_s=(\frac{9}{4}\pi)^{1/3}$. $\psi_x(N)$ can be evaluated by direct summation (Table II).

III. DISCUSSION

We see from Tables I and II that as the number N increases, $\psi_x(N)$ attains the value 1 much more rapidly than $\psi_c(N)$. For example, when $N=54$, $\psi_x=0.94$ and $\psi_c=0.59$ for α chosen to be 0.25. In expression (8) we have excluded the "self-interaction" terms $k_i=k_j$. Their absence accounts for the small values of ψ_x when N is small. Such terms are present in the exchange energy of Kohn and Sham and are subtracted away by the self-interaction terms of the direct Coulomb energy. In other words, for small N, ϵ_x is a better approximation of the true situation than what we see in Table II. From these considerations we can conclude that it is not surprising to get a proportionally better value of the exchange energy than that of the correlation energy even though the same approximations are used in the functional $E_{xc}[n]$ [Eq. (1)]. It is quite amazing that in such model calculations, the correlation energy of an infinite system at average atomic density is indeed about twice that of the finite system of $N\simeq 14$–28, corresponding to medium sized atoms. This may be accidental, but the idea of the "softness" of an infinite system and the "hardness" of a finite system is well demonstrated.

TABLE I. Correlation energy $\epsilon_{\text{corr}}(\alpha, N)$.

	$\alpha=0.25$		$\alpha=0.18$	
N	ϵ_{corr}(Ry)	$\psi_c(N)$	ϵ_{corr}(Ry)	$\psi_c(N)$
14	−0.1183	0.5757	−0.1263	0.5149
38	−0.1316	0.6404	−0.1430	0.5830
54	−0.1219	0.5932	−0.1316	0.5365
66	−0.1469	0.7148	−0.1629	0.6641
114	−0.1764	0.8584	−0.2029	0.8272
162[a]	−0.184	0.895	−0.214	0.872
∞	$\epsilon_{\text{Huby}}=-0.21055$	1	$\epsilon_{\text{Huby}}=-0.2453$	1

[a] Evaluated by the Monte Carlo method.

Thus a major obstacle in using expressions derived for an infinite system in the calculation of properties of a finite system comes from the discrete nature of the excitation spectrum. This is true not only in the local-potential approximation. These ideas had also been commented upon by Sinanoğlu,[8] who said "The behavior of the electron correlation in atoms and molecules is very different from that in a uniform electron gas due to geometry, finite spacings of orbital levels, exclusion effects, and the very different nature of the potentials responsible for correlation in the two distinct types of systems." It seems to us that in the above statement other factors can either be eliminated by a correct formulation or else be indirectly related again to the finite spacing of the levels. Take exclusion effects as an example. It has been observed by Kelly[4,11] that in the calculation of the correlation energy of atomic systems using Brueckner-Goldstone perturbation theory,[12,13] there is a class of exclusion-principle-violating diagrams which are among the major contributors. These diagrams do not contribute in the homogeneous interacting infinite electron gas systems. Perhaps the correct way is to evaluate the exchange and correlation energies ϵ_{xc} in Eq. (1) for the true atomic orbitals instead of using the expressions of an interacting infinite system. The

TABLE II. Exchange-energy ratio $\psi_x(N) = \epsilon_x(N)/\epsilon_x(\infty)$.

N	$\psi_x(N)$
14	0.3257
38	0.5941
54	0.9423
66	1.1576
∞	1

TABLE III. Relation between α and r_s. For a given α, r_s is obtained from equating (a) $\epsilon_{\text{Huby}}(\alpha) = \epsilon_{\text{GB}}(r_s)$, (b) $\epsilon_{\text{Huby}}(\alpha) = \epsilon_{\text{GBR}}(r_s)$, (c) $\epsilon_{\text{B}}(\alpha) = \epsilon_{\text{GB}}(r_s)$, (d) $\epsilon_{\text{B}}(\alpha) = \epsilon_{\text{GBR}}(r_s)$.

	r_s			
α	(a)	(b)	(c)	(d)
0.18	0.091	0.190	0.104	0.215
0.20	0.115	0.240	0.128	0.266
0.25	0.172	0.360	0.200	0.416

rapid variation of electron densities near the center of an atom is certainly another source of error in the local-effective-potential approximation, but perhaps it is less severe than what has been pointed out.

Ma and Brueckner[7] commented that higher terms in the gradient expansion give an even larger estimate than a factor of 2 in the correlation energies of atoms. It led them to conclude that a gradient expansion gives diverging results for atomic systems. Their study was based on infinite electron gas expressions and the discrete nature of atomic levels was not considered. If the latter is accounted for, it is not clear that their conclusion on the gradient-expansion approach will remain as it is.

Finally we repeat our previous remark on the local-effective-potential approximation of the Kohn-Sham self-consistent scheme as applied to the study of atomic systems. The method has been proved to be a simple efficient scheme in getting excellent electron densities. Its estimates of energies are fairly good except for the correlation energy. Even the latter gets better for larger systems. In large atoms or in molecules where a detailed Hartree-Fock calculation and the beautiful scheme of Sinanoğlu in calculating correlation energies[14] become tedious, this scheme may prove to be the most useful. The difficulty of discrete excitation levels does not exist in a good metal. Its application to the study of a metallic system is the therefore quite successful.[15]

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APPENDIX A: SCREENING CONSTANT α

The correlation energy of a high-density homogeneous interacting electron gas has been calculated by Gell-Mann and Brueckner[6] by summing over all the ring diagrams (R) [Fig. 1(a)], giving

$$\epsilon_{\text{GBR}}(r_s) = 0.0622 \ln r_s - 0.050 \ . \tag{A1}$$

The exchange diagrams contribute very little in the high-density limit. The second-order exchange diagram has been estimated to be about -0.046 Ry. Including this, the correlation energy becomes

$$\epsilon_{\text{GB}}(r_s) = 0.0622 \ln r_s - 0.096 \ . \tag{A2}$$

In the case of a screened Coulomb interaction [Eq. (2)] the second-order ring-diagram contribution is given in Eq. (4). At very high densities, an approximate result can be obtained (using a similar procedure described by Brueckner[16]):

$$\epsilon_{\text{B}}(\alpha) = -0.0622\{\ln[1 + (2k_F/\alpha)^2] - 1\} \ . \tag{A3}$$

The exact expression $\epsilon_{\text{Huby}}(\alpha)$ is given by Huby[10] [Eq. (7)].

We shall estimate the value of α at atomic densities by equating $\epsilon_{\text{B}}(\alpha)$ or $\epsilon_{\text{Huby}}(\alpha)$ to $\epsilon_{\text{GBR}}(r_s)$. This procedure is equivalent to the random-phase-approximation (RPA) result of replacing the contribution of the polarization diagrams by an effective screened potential (Fig. 2). On the other hand, if we choose α by equating these with $\epsilon_{\text{GB}}(r_s)$, we include the corresponding exchange contribution of these polarization diagrams as well. Hence in Sec. II although we only discuss the second-order ring diagram for a screened Coulomb interaction, we have already approximately included all the ring diagrams and their exchange counterparts. α obtained from these various comparisons are listed in Table III. We see that for $\alpha \sim 0.18-0.25$, the corresponding r_s are within the reasonable range found in atoms which is about 0.2–0.4. [For example, the second peaks in the radial density curves of Ne and Ar (Figs. 2 and 3 of I) correspond to $r_s \sim 0.35$ and 0.20, respectively.]

Equating $\epsilon_{\text{B}}(\alpha)$ with $\epsilon_{\text{GB}}(r_s)$, we get

$$\alpha \sim 0.56\, r_s^{1/2} \ . \tag{A4}$$

If we include only the ring diagrams, we compare

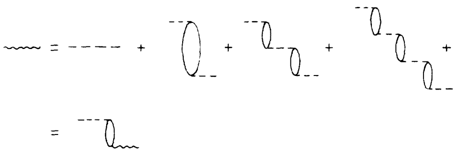

FIG. 2. Summation of polarization parts.

TABLE IV. Correlation-energy calculation for $N = 38$, $\alpha = 0.25$; contribution from shells outside $L = 20$ is -0.0039 Ry giving a total estimate of $\epsilon_{\text{corr}} = -0.1316$ Ry.

Shell number L	Type	Multiplicity	k_m^2	$E_C(L)$ (Ry)[a]
1	(111)	8	3	$-0.038\,998$
2	(200)	6	4	$-0.051\,241$
3	(210)	24	5	$-0.085\,346$
4	(211)	24	6	$-0.101\,744$
5	(220)	12	8	$-0.105\,668$
6	(221)	24	9	$-0.110\,767$
	(300)	6	9	$-0.111\,978$
7	(310)	24	10	$-0.115\,489$
8	(311)	24	11	$-0.118\,215$
9	(222)	8	12	$-0.118\,885$
10	(320)	24	13	$-0.120\,544$
11	(321)	48	14	$-0.123\,060$
12	(400)	6	16	$-0.123\,260$
13	(322)	24	17	$-0.123\,930$
	(410)	24	17	$-0.124\,588$
14	(330)	12	18	$-0.124\,867$
	(411)	24	18	$-0.125\,413$
15	(331)	24	19	$-0.125\,879$
16	(420)	24	20	$-0.126\,268$
17	(421)	48	21	$-0.126\,929$
18	(332)	24	22	$-0.127\,213$
19	(422)	24	24	$-0.127\,426$
20	(430)	24	25	$-0.127\,614$
	(500)	6	25	$-0.127\,660$

[a] $E_C(L)$ is the correlation energy evaluated by summing k_m up to the Lth shell.

it with $\epsilon_{\text{GBR}}(r_s)$, giving

$$\alpha \sim 0.39\, r_s^{1/2} . \tag{A5}$$

It is interesting to compare these values with the RPA estimate of Pines[17] which gives $\alpha \sim 0.353\, r_s^{1/2}$, and with the Thomas-Fermi value which gives $\alpha \sim 0.81\, r_s^{1/2}$.

APPENDIX B: EVALUATION OF CORRELATION ENERGY ϵ_{corr} FOR FINITE SYSTEMS

When the number of particles N in the system is small, we can evaluate $\epsilon_{\text{corr}}(\alpha, N)$ of the model system through term by term summation [Eq. (5)]. For a given N, we first calculate the "averaged" k_F defined by Eq. (3). The $\vec{k}$ space is a lattice of simple cubes of sides $k_0 = 2\pi/a$, where $a^3 = \Omega =$ volume of the model system. All points within a sphere of radius k_F are occupied, and the k_m must lie outside this sphere. For a fixed k_m we can evaluate all other summations. The Pauli principle and momentum conservation must be satisfied. Staring from a point $\vec{k}_m$ closest to the Fermi sphere, we finally add all the terms of different $\vec{k}_m$ points as $|k_m|$ becomes larger and larger. Let us characterize $\vec{k}_m$ by (abc) corresponding to all points in $\vec{k}$ space having coordinates formed from all combinations of the plus and minus values of a, b, and c and their rearrangements in different orders. The total number of such $\vec{k}_m$ points of the type (abc) will be denoted by "multiplicity." $E_C(L)$ is the value of the correlation energy obtained by summing $\vec{k}_m$ up to the Lth shell. A sample case of $N = 38$ is given in Table IV. In all cases the summation over increasing magnitude of $|k_m|$ converges rapidly. It is, therefore, possible to carry out the explicit summation up to $|k_m| \leq m k_F$, where m is a suitably large number depending on the rate of convergence, and add to this the estimated contribution of all the rest $\vec{k}_m$ points outside mk_F. In estimating the latter, we can replace the summation over $\vec{k}_F$ by integration, because now we are far away from the origin and the $\vec{k}$ points are numerous. There is no more vanishing denominator in the integrand. The details of such estimation will not be presented here. In all cases, m is chosen such that the upper bound of the contribution from the $\vec{k}_m$ summation outside mk_F never exceeds -0.004 Ry.

The above method becomes tedious as the number of particles N increases beyond 100. The Monte Carlo method was used in the evaluation of ϵ_{corr} for the case $N = 162$.

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Quark-Molecule Calculations

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Electronic structures of hypothetical molecules containing quarks, or fractionally charged particles, are treated. By regarding the quark charge Q as a continuous variable, approximations satisfying a consistency condition at small-Q values are formulated. Their validity is checked with the exact solutions of the one-electron two-center problem and applied to two-electron two-center problems of H^--quark and He-quark molecules.

I. INTRODUCTION

The idea of Gell-Mann and Zweig[1] about quarks or hypothetical elementary particles bearing fractional electrical charges initiated a series of experiments[2] in search of such particles—so far without success. Quark-search experiments may be classified into two types: namely, those of the first type making use of high-energy quarks expected to be produced by accelerator beams or cosmic rays and those of the second type which make use of thermalized quarks. Experiments of the second type usually rely on some assumptions about the physicochemical properties of thermalized quarks. Although the existence of quarks themselves is an unsettled fundamental question of theoretical physics, the physicochemical properties of thermalized quarks, if they do exist, are governed by a well-established law of nature, namely, quantum mechanics and quantum chemistry. This is particularly the case because the failure of high-energy accelerator experiments in the search for quarks has set mass limits on quarks well over the proton mass[2] so that the Born-Oppenheimer approximation can be applied with a high degree of confidence for quantum-mechanical calculations of the properties of molecules containing quarks. If quantum-chemical calculations of quark molecules are performed reliably and extensively, they will provide sound bases for quark-search experiments of the second type and will also supply useful information for the design of further experimentations of this type. Predictions about the binding energy of quarks to, or the quark affinity for, various ordinary matter will provide valuable information for the design of such experiments.

Quark chemistry in the broadest sense will have to treat all nuclear species bearing charges of $Z = \pm \frac{1}{3}Ne$, where e is the magnitude of the electronic charge and N can be any integer. In this paper, however, we shall consider only particles bearing charges of $+Qe$, $0 \leq Q \leq 1$. On the other hand, our treatment will not be restricted to the quarks of $Q = \frac{1}{3}$ or $\frac{2}{3}$ as suggested by Gell-Mann and Zweig,[1] but shall regard Q as a continuous variable. Such a treatment will be useful to gain more insights into the nature of quark-containing molecules and hopefully of hydrides as an extreme case of $Q = 1$.