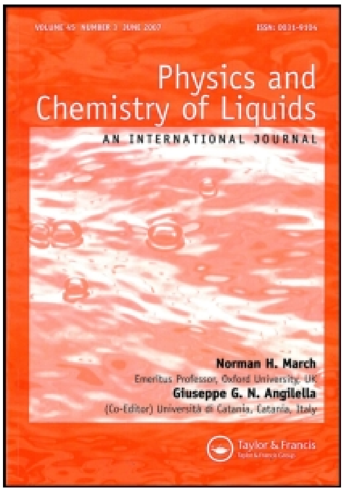
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Inhomogeneous electron liquids generated by Coulomb confinement of electrons with and without interparticle repulsions

N. H. March[abc]

[a] Department of Physics, University of Antwerp, Antwerp, Belgium [b] The Abdus Salam International Centre for Theoretical Physics, Italy [c] Oxford University, UK

To cite this Article March, N. H.(2009) 'Inhomogeneous electron liquids generated by Coulomb confinement of electrons with and without interparticle repulsions', Physics and Chemistry of Liquids, 47: 1, 45 — 60

To link to this Article: DOI: 10.1080/00319100802436489

URL: http://dx.doi.org/10.1080/00319100802436489

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Physics and Chemistry of Liquids
Vol. 47, No. 1, February 2009, 45–60

Inhomogeneous electron liquids generated by Coulomb confinement of electrons with and without interparticle repulsions

N.H. March[abc]*

[a]*Department of Physics, University of Antwerp, Antwerp, Belgium;* [b]*The Abdus Salam International Centre for Theoretical Physics, Trieste, Italy;* [c]*Oxford University, Oxford, UK*

(*Received in final form 28 August 2008*)

The inhomogeneous electron liquid created through Coulomb confinement by a single-centre potential energy $-Ze^2/r$ remains central to the fundamental $1/Z$ expansion: a pillar of analytic atomic theory. Therefore, some recent progress in this area of non-relativistic quantum mechanics is first discussed, the main focus being the Feynman propagator. The closely related Slater sum is also treated, differential equations being cited in both three and two dimensions. The effect of interparticle interactions on the density of the electron liquids will next be considered in two areas: (i) for models of He-like atomic ions with nuclear charge Ze where analytic ground state electron densities can be obtained, as well as the exact differential equations they satisfy, and (ii) fine-tuning of Hartree–Fock densities for four spherical atoms, Be, Ne, Mg and Ar. In (ii), a semi-empirical framework is now available in which the experimental ionisation potential replaces that of Koopmans. Densities having almost QMC quality are thereby available. Finally, the inhomogeneous electron liquids in short linear chains of H nuclei stabilised by one electron plus an intense magnetic field along the chain axis will be treated, fields considered being as found at the surfaces of some neutron stars.

Keywords: inhomogeneous electron liquids; Coulomb confinement; interparticle repulsions

1. Background and outline

A pillar of atomic theory built on Schrödinger's equation is the so-called $1/Z$ expansion (see also Appendix A). Here, the leading term is purely hydrogenic in character and it, therefore, continues to be of considerable significance to obtain compact analytical expressions for fundamental quantum mechanical properties connected to the inhomogeneous electron density.

Therefore, in the present article, Section 2 is concerned with analysis on three such basic quantities, namely, the off-diagonal Feynman propagator (Equation (1)), the corresponding Green function, and the so-called Slater sum defined, for example, in Equation (11).

---

*Email: giuseppe.angilella@ct.infn.it

ISSN 0031–9104 print/ISSN 1029–0451 online

DOI: 10.1080/00319100802436489
http://www.informaworld.com

Following this discussion of properties of the bare Coulomb potential energy, Section 3 is devoted to the effect of electron–electron interaction on solvable two-electron atomic models, the primary focus being on ground-state electron densities given such model non-relativistic Hamiltonians.

To this point, all considerations are from first principles. But Section 4 then sets out a semiempirical route to fine-tune Hartree–Fock (HF) ground-state electron densities, the experimental ionisation potential being inserted. Examples are cited for some spherical atoms such as Ne and Mg.

Section 5 then effects some generalisations of the above treatment of atoms to the chain-like molecular ions H_2^+, H_3^{2+} and H_4^{3+} with and without applied magnetic fields along the internuclear axes. Again, analytic progress proves possible. Finally Section 6 constitutes a summary, plus some suggestions for future studies which should prove fruitful.

2. Off-diagonal Feynman propagator, Green function and Slater sum for the bare Coulomb potential energy $-Ze^2/r$

Here we shall summarise recent progress on the off-diagonal Feynman propagator and the associated Green function for a bare Coulomb potential energy $-Ze^2/r$ [1]. We define the Feynman propagator $K(\mathbf{r}_1,\mathbf{r}_2,t)$ in terms of Coulomb wave functions $\psi_n(\mathbf{r})$ and corresponding energies ϵ_n as

$$K(\mathbf{r}_1,\mathbf{r}_2,t)=\sum_n \psi_n(\mathbf{r}_1)\psi_n^*(\mathbf{r}_2)\exp(-i\epsilon_n t). \tag{1}$$

With the introduction of the variable $\beta = it$ the propagator has the form of a statistical mechanical density matrix $C(\mathbf{r}_1,\mathbf{r}_2,\beta)$, where $\beta=(k_B T)^{-1}$, the reciprocal of the thermal energy.

Howard and March consider the limiting off-diagonal case $C(r,0,\beta)$ and write

$$C(r,0,\beta)=(2\pi\beta)^{-3/2}\exp(-r^2/2\beta)+O(Z), \tag{2}$$

where the first term on the RHS evidently comes from the free-particle Feynman propagator, i.e. the limit $Z\to 0$. The term of order Z in Equation (2), say C_1, has the explicit form

$$C_1(r,0,\beta)=\frac{Z}{2\sqrt{2\pi\beta}}\frac{\exp\left(-r^2/2\beta\right)}{r}\left[i\mathrm{erf}\left(\frac{ir}{\sqrt{2\beta}}\right)\right]. \tag{3}$$

2.1. *Results for Green function*

The corresponding Green function $G(r,0,-E)$, related to C by a Laplace transform,

$$\mathcal{L}C(r,0,\beta)=G(r,0,-E), \tag{4}$$

is readily shown to satisfy the integral equation

$$G(r,0,-E)=\frac{\exp\left(-\{2E\}^{(1/2)}r\right)}{r}+\int\frac{\exp\left(-\{2E\}^{(1/2)}r\right)|\mathbf{r}-\mathbf{r}_1|}{|\mathbf{r}-\mathbf{r}_1|}\frac{Z}{r_1}G(r_1,0,-E)\mathrm{d}\mathbf{r}_1. \tag{5}$$

This integral equation must have as its solution, but unfortunately in integral form only to date:

$$G(r,0,-E)=\frac{-ik^2}{16\pi}\int_0^\infty \mathrm{d}s\exp(iZs)\mathrm{cosech}^2(ks)\exp\left\{\frac{ik}{2}r\coth(ks)\right\}J_0(0), \tag{6}$$

which is equivalent to the various known integral expressions of the Green function for the H atom (e.g. a simple change of variable brings it to the result given by Dura and Kleinert [2]. Obviously, expanding $\exp(iZs)$ in Equation (6) to $O(Z)$, one must regain the closed analytic form for $C_1(r,0,\beta)$ given in Equation (3) above.

2.2. *Two-dimensional case of $V = -Ze^2/r$*

For the potential $-Ze^2/r$ but now in 2D, we know the analogue of the first term on the RHS of Equation (2) for the free-particle limit. It is

$$C_0^{2\mathrm{D}}(\mathbf{r},\mathbf{r}',\beta)=\frac{1}{2\pi\beta}\exp\left(-\frac{|\mathbf{r}-\mathbf{r}'|^2}{2\beta}\right) \tag{7}$$

and the corresponding Green function $G_0^{2\mathrm{D}}$ is given in terms of Hankel functions by

$$G_0^{2\mathrm{D}}(\mathbf{r},\mathbf{r}',E)=-(2m/\hbar^2)(i/4)H_0^{(1)}(k|\mathbf{r}-\mathbf{r}'|), \tag{8}$$

where $k^2=2mE/\hbar^2$, and $H_0^{(1)}$ is the customary Hankel function [3]. The corresponding asympotic form for the scattered wave function is readily shown to be, in the 2D case under discussion:

$$\psi_k(\mathbf{r})_{r\to\infty}\to\exp(ikx)+\frac{2m}{\hbar^2}\left\{\frac{i}{k}\right\}^{(1/2)}\frac{\exp(ikr)}{r\frac{1}{2}}f_k(\theta), \tag{9}$$

the last term being the outgoing scattered wave with $f_k(\theta)$ the scattering amplitude.

For $Z\neq 0$, one can write an integral form of the Green function analogous to Equation (6), and having the off-diagonal integral form [4]

$$G^{2\mathrm{D}}(r,0,E)=\frac{k}{4\pi}\int_0^\infty \mathrm{d}s\exp(iZs)\mathrm{cosech}(ks)\exp\left[\frac{1}{2}ikr\coth(ks)\right] \tag{10}$$

but to the writer's knowledge this integral can only presently be performed in the free-particle limit $Z\to 0$, when the Hankel function $H_0^{(1)}(kr)$ must be recovered, as in Equation (8) above.

2.3. *Slater sum for Coulomb confinement*

The Slater sum, by definition, is the diagonal element of the canonical density matrix $C(\mathbf{r},\mathbf{r}_0,\beta)$, namely

$$S(\mathbf{r},\beta)=C(\mathbf{r},\mathbf{r}_0,\beta)\big|_{\mathbf{r}_0=\mathbf{r}}. \tag{11}$$

For central field confinement by the Coulomb potential energy $V(r)$:

$$V(r) = -\frac{Ze^2}{r}, \tag{12}$$

March and Murray [5] derived for the s-wave only component, $S_0(r,\beta)$ of the above Slater sum (11) the partial differential Equation [5, Equation (4.77)], in atomic units:

$$\frac{1}{8}\frac{\partial^3}{\partial r^3}(r^2 S_0) - \frac{\partial^2}{\partial r \partial \beta}(r^2 S_0) + \frac{Z}{r}\frac{\partial}{\partial r}(r^2 S_0) - \frac{ZS_0}{2} = 0. \tag{13}$$

If we now introduce into Equation (13) the spatial generalisation of Kato's theorem [6] derived by the present author [7], namely,

$$\frac{\partial S}{\partial r} = -2ZS_0, \tag{14}$$

we readily find [8]

$$\frac{1}{2r}\frac{\partial}{\partial r}\left(r^2 \frac{\partial S}{\partial r}\right) - \frac{1}{4}\frac{\partial S}{\partial r} = \frac{1}{8}\frac{\partial^3}{\partial r^3}(rS_0) - \frac{\partial^2}{\partial r \partial \beta}(r^2 S_0). \tag{15}$$

This Equation (15) evidently relates the total Slater sum S for the potential (12) to its s-state only component S_0. The electron density $n(r,E)$ is related to $S(r,\beta)$ by Laplace transform inversion [5].

2.4. *Two-dimensional Slater sum for Coulomb confinement*

As a starting point let us consider the Slater sum $S(r,\beta)$ in two dimensions. We will work by analogy with the 3D case, for which the partial differential equation for the Slater sum was obtained independently by Cooper [9] and by Pfalzner, *et al.* [10]. The result is

$$\frac{1}{8}S''' + \frac{S''}{2r} + \frac{S'}{4r^2} - \left(V + \frac{\partial}{\partial \beta}\right)S' + \frac{1}{2}V'S = 0. \tag{16}$$

This equation is solved by the $\beta \to \infty$ form of $S(r,\beta)$ for the 3D Coulomb potential, apart from a multiplying constant which does not affect the linear, homogeneous Equation (16).

2.4.1. *Differential equation for bound-state Slater sum $S(r,\beta)$ for potential $V = -Ze^2/r$ in two dimensions*

We expect for slow spatial variations the Lehmann–March limiting result [11]

$$-\left(V(r) + \frac{\partial}{\partial \beta}\right)S' - \left(1 - \frac{D}{2}\right)\frac{\partial V}{\partial r}S = 0 \tag{17}$$

in D dimensions. The 3D result in Equation (11) above includes Equation (17), but additionally the terms

$$\frac{1}{8}S''' + \frac{1}{2r}S'' + \frac{1}{4r^2}S'$$

for the Coulomb case.

For the D-dimensional harmonic oscillator, Howard and March [12] write

$$\frac{\hbar^2}{8m}\frac{\partial}{\partial r}(\nabla^2 S) - \left[V(r) + \frac{\partial}{\partial \beta}\right]S' - \left(1 - \frac{D}{2}\right)\frac{\partial V}{\partial r}S = 0, \tag{18}$$

which includes Equation (17) but $\frac{\partial}{\partial r}(\nabla^2 S)$ does not appear in that equation. In two dimensions we have

$$\frac{\partial}{\partial r}\nabla^2 S = \frac{\partial}{\partial r}\left[S'' + \frac{1}{r}S'\right] = S''' + \frac{1}{r}S'' - \frac{1}{r^2}S', \tag{19}$$

which would be there in the 2D special case of Equation (18). Hence, for the 2D Coulomb field, we propose the differential equation for the Slater sum $S(r, \beta)$, in atomic units, as

$$\frac{1}{8}\left[S''' + \frac{1}{r}S'' - \frac{1}{r^2}S'\right] - \left[V(r) + \frac{\partial}{\partial \beta}\right]S' - \left(1 - \frac{D}{2}\right)\frac{\partial V}{\partial r}S = 0. \tag{20}$$

So far, no closed analytic solution of this Equation (20) exists. Again, the electron density $n(r, E)$ is related to $S(r, \beta)$ [5].

3. Solvable two-electron He-like models for ground-state electron densities

Having dealt with some properties of the bare Coulomb potential, we turn now to the role of interelectronic repulsion. The natural starting point is then that of two-electron He-like models, of which we shall single out three areas in which recent progress has proved possible.

3.1. *Chandrasekhar three-parameter ground-state wave function for He-like atomic ions*

We start with the Chandrasekhar (Ch) wave function [14] for the ground-state of He-like atomic ions. This has the explicit spatial form $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ given by

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \mathcal{N}[1 + cr_{12}][\exp(-ar_1 - br_2 + \exp(-br_1 - ar_2)]. \tag{21}$$

Here $\mathcal{N}$ is a normalisation factor while a, b and c are the three parameters which Ch proposed to determine variationally. Later work by Howard and March [15] gave a table of a, b and c for Z from 2 to 10 obtained by a non-variational procedure. Table 1 summarises their results from $Z = 1$ to 3, and for larger Z a and b vary remarkably linearly with atomic number Z, while for $Z > 3$, c is almost constant. As shown by Howard *et al.* [13], this wave-function (21) has the considerable merit that the ground-state electron density,

$$\rho(r) = 2\int \Psi^2(\mathbf{r}, \mathbf{r}_2)\mathrm{d}\mathbf{r}_2, \tag{22}$$

can be obtained analytically (see Equation (3) in [13]).

The Hamiltonian for which Ψ of Ch is the exact ground eigenstate can be shown to be of the form

$$H_{\mathrm{Ch}} = \frac{-\hbar^2}{2m}\left[\nabla_1^2 + \nabla_2^2\right] - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + u(\mathbf{r}_1, \mathbf{r}_2). \tag{23}$$

Table 1. Howard–March non-variational estimates of parameters a, b and c in Chandrasekhar wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ given in Equation (21) for He-like atomic ions, in range of atomic number Z.

Z	1	2	3
a	0.478	1.436	2.362
b	1.075	2.208	3.299
c	0.3121	0.2924	0.2770

Note: a and b vary almost linearly with Z, while c becomes largely independent of Z after $Z \sim 5$ (after Howard and March [13]).

While for He itself $u = e^2/|\mathbf{r}_1 - \mathbf{r}_2|$, for the Ch wave function u is not simply a function of $|\mathbf{r}_1 - \mathbf{r}_2|$, the explicit form being given in [16].

3.2. *Schwartz density of He-like atomic ions in (non-relativistic) limit*

Let us begin by discussing analytically the long-range asymptotic behaviour of the ground-state electron density in the (non-relativistic) series of He-like ions as a function of atomic number Z.

Going back at very least to the work of Hoffmann-Ostenhof and Hoffmann-Ostenhin [17], it has been known that, using atomic units, the ground-state density of rare gas atoms with spherical electron density $\rho(r)$ decays at sufficiently large r as

$$\rho(r) \sim Ar^n \exp(-2\{2I\}^{(1/2)}r) : r \to \infty, \tag{24}$$

where I denotes the ionisation potential.

Furthermore, in the early work of Schwartz [18] it was found that in the (still non-relativistic) limit of large Z,

$$\rho(r) = \frac{2Z^3}{\pi}\left[1 + \frac{2}{Z}\chi(r)\right]\exp(-2Zr), \tag{25}$$

where $\chi(r)$ was obtained explicitly. Subsequently March and Pucci [19] utilised Equation (25) with the Schwartz analytic form of $\chi(r)$ to show that, again for Z sufficiently large, $(2I)^{(1/2)} \sim Z - 5/8$. In Equation (24), $n \sim -(3/4)Z^{-1}$ and $A = (2Z^3/\pi)$ $[1-(3/4Z) \log Z + O(Z^{-1})]$.

3.3. *Modified s-wave model of He atom with ultrastrong radial correlation*

In an earlier study, Howard and March [20] (referred to as HM below) proposed an analytic ground-state electron density $\rho(r)$ starting from the s-wave model of He going back at least to Temkin [21]. Subsequently Ancarani [22] has constructed, but by purely numerical procedures, a variational approach for this s-wave model, which yields a lower energy than the HM result. This clearly means, as Ancarani [22], and somewhat

Table 2. Comparison of experimental ionisation potentials (in a.u.) with Koopmans approximate values of Be, Ne, Mg and Ar neutral atoms.

Atom	Z	I_K	$I_{\exp t}$	I_{NR}
Ne	10	0.8504	0.7925	0.7945
Ar	18	0.5910	0.5792	0.5822
Be	4	0.3093	0.3426	0.3443
Mg	12	0.2531	0.2810	0.2807

Note: Table constructed from data by Cordero *et al.* [27]. I_{NR} shows small relativistic 'corrections' made to $I_{\exp t}$.

earlier Serra [23] recognised, that the HM analytic $\rho(r)$ is not the ground-state electron density of the He s-wave model.

This situation has led Amovilli *et al.* [24] to derive an exact non-relativistic Hamiltonian, with strong radial correlation plus Coulomb confinement, for which the HM $\rho(r)$ is the exact ground-state density.

The HM wavefunction is readily expressed as

$$\Psi(r_>, r_<) = C\exp[-(Z-1)r_> - Zr_<], \tag{26}$$

where $r_> = (r_1 + r_2 + |r_1 - r_2|)/2$ and $r_< = (r_1 + r_2 - |r_1 - r_2|)/2$. The point to be emphasised at this stage is that this ground-state wave function (26) has a discontinuity in its derivative at $r_1 = r_2$. Therefore, Amovilli *et al.* [24] have, considering this discontinuity, shown that the HM wave function (26) is the exact ground-state wave function of the 'modified s-wave (ms)' Hamiltonian defined by

$$\mathrm{H}_{ms} = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_2} + \frac{1}{r_>} + \delta(r_1 - r_2), \tag{27}$$

the modification of the original He-like s-wave model being due to the presence of the δ function in H_{ms}. This model Hamiltonian, of interest in its own right since both density $\rho(r)$ and its off-diagonal generalisation to the correlated first-order density matrix [16] are known, is also of potential significance in the search for a Schrödinger-like equation for the pair density amplitude [25], as stressed by Amovilli *et al.* [16].

As a two-electron wave function dependent only on r_1 and r_2, the HM form (26) satisfies automatically the angular momentum requirements $\ell_1 = \ell_2 = L = 0$.

Let us stress here that the exact Hamiltonian H_{ms} in Equation (27) has Coulomb confinement plus kinetic energy operators exactly as in the He-like atomic ions, but differs because the real electron–electron repulsion potential energy e^2/r_{12} has been replaced by the ultrastrong but purely radial correlation given explicitly by the final two terms of Equation (27). The second point of specific interest in the present context is that the density $\rho(r)$ of HM is known [20] to satisfy the exact differential equation

$$(a_0 + a_1 r + a_2 r^2)\rho'' + (b_0 + b_1 r + b_2 r^2)\rho' + (c_0 + c_1 r + c_2 r^2)\rho = 0 \tag{28}$$

with coefficients given in Table 2 of Howard and March [20]. Moreover, the entanglement of the HM wave function (26) is demonstrated directly from the one-particle density matrix γ satisfying $\gamma^2 < \gamma$ obtained subsequently by Amovilli and March [24].

In view of the present intractability of the He atom ground-state wave function from the point of view of exact analytic theory, it would be of considerable interest if generalisations of the modified *s*-wave Hamiltonian (27) exhibited here for Coulomb confinement could be found for other interparticle interactions. For the simpler case of harmonic confinement, Holas *et al.* [26] have already presented a quite general integral for the inhomogeneous density $\rho(r)$ and its off-diagonal form $\gamma(\mathbf{r}_1, \mathbf{r}_2)$ for a model two-electron atom with arbitrary inter-Fermion repulsion $u(\mathbf{r}_{12})$.

4. Fine tuning of HF ground-state electron densities, with experimental ionisation potential inserted

In this section, we will briefly summarise recent progress on ground-state electron densities of some light spherical atoms such as Ne and Mg [27]. Starting from a modification of HF theory, it emerges that electron densities approaching quantum Monte Carlo (QMC) quality can be obtained: by inserting one piece of empirical data, namely, the experimental ionisation potential (when corrected for small relativistic effects).

Following the approach of Cordero *et al.* [27], one makes two changes in the conventional HF theory for neutral atoms. Firstly, one allows the (integral) nuclear charge Ze to become non-integral, say $Z'e$. Secondly, the Kato electron-nuclear cusp condition is to be imposed by means of a scaling parameter, λ, of the form

$$\rho_\lambda(r) = \lambda^3 \rho(\lambda r), \tag{29}$$

where for the neutral atoms under consideration:

$$\int \rho(r) \mathrm{d}\mathbf{r} = Z. \tag{30}$$

Always, Equation (29) and (30) ensure that the number of electrons in the 'fine-tuned' HF density $\rho_\lambda(r)$ is equal to Z for any choice of the scaling factor λ.

We anticipate the results [27] to be summarised below by saying that the high quality of atomic HF ground-state electron densities, already known to Møller and Plesset [28] in their pioneering studies, is evident since the non-integral Z' turns out to be very near to Z and λ proves to be near to unity.

4.1. *Results for some light neutral atoms*

Table 2 records first of all the HF ionisation potential I_K, where K denotes the Koopmans value, compared with the experimental value, plus its slightly changed value when corrected for relativity. Taking the latter point first, the last two columns are seen to differ only in the third decimal place for these four light neutral atoms.

Of course, the change from the Koopmans ionisation potential I_K to the empirical value I_{NR} is significant, and corrects the asymptotic large r behaviour of the ground-state electron density appropriately. The densities of Ne and Ar are seen then from Table 2 to fall off somewhat less rapidly at large r than their HF counterparts, whereas the opposite situation obtains for the (also spherical) atoms Be and Mg.

Table 3 shows the key parameters Z' and λ in the fine-tuning procedure for HF ground-state densities. The table makes it clear that the HF solutions obtained by numerical integration of radial Schrödinger equations, without, therefore, any appeal to

Table 3. Table taken from data by Cordero *et al.* [27].

Atom	Non-integral Z'	$\lambda = Z/Z'$
Ne	9.91	1.0088
Ar	17.98	1.0011
Be	4.13	0.9692
Mg	12.10	0.9921

Note: λ is a scaling factor appearing in Equation (29).

basis sets, are for (slightly) negative ions for Ne and Ar, and that the cases of Be and Mg correspond to weakly positive ions.

Tables in [27] demonstrate in some detail that it turns out by direct comparison of various averages with QMC data available in the literature that the fine-tuning of HF electron densities by the method of [27] is leading to results of QMC quality for these inhomogeneous electron liquids.

5. Inhomogeneous electron liquids in the molecular ions H_2^+, H_3^{2+} and H_4^{3+} with and without applied magnetic fields

So far we have been concerned with one-centre Coulomb confinement. In this section we turn to summarise some analytic progress that proves possible for three hydrogen molecular ions. It is then natural to start with the simplest case H_2^+, with and without an applied magnetic field.

5.1. *H_2^+ in zero magnetic field*

In Section 2.3, we have utilised for the one-centre Coulomb field and for closed shells, the spatial generalisation of Kato's theorem which allows the ground-state density $\rho(r)$ [7] to be expressed quite explicitly in terms of the *s*-state density $\rho_s(r)$, plus the charge Ze entering the Coulomb potential energy $-Ze^2/r$:

$$\rho(r) = \frac{2Z}{a_0}\int_r^\infty \rho_s(t)\mathrm{d}t. \tag{31}$$

The purpose of this short section (see also Appendix B) is to point out, and to briefly summarise, the result [29] that for the two-centre bare Coulomb field problem appropriate to the ground-state of the molecular ion H_2^+ the electron density $\rho(\mathbf{r}, R)$, with R the internuclear separation, is determined solely by the electron density on the plane perpendicularly bisecting the bond axis.

As shown by Burrau [30] (see also [31]), the ground-state wave function ψ separates in dimensionless confocal elliptic coordinates ξ and η to yield for the H_2^+ molecular ion,

$$\psi(\xi, \eta, R) = X(\xi)Y(\eta). \tag{32}$$

With r_1 and r_2 measured from protons 1 and 2, respectively, one has the definitions

$$\xi = \frac{r_1 + r_2}{R}, \quad \eta = \frac{r_1 - r_2}{R}. \tag{33}$$

The ordinary differential equations for $X(\xi)$ and $Y(\eta)$ are set out in Appendix B.

From Equation (32), it is clear that, on the mirror plane, $r_1 = r_2 = r$ say, and $\eta = 0$. Thus the mirror plane density $\rho(\xi, \eta = 0) \equiv \rho_0(\xi)$ is given by

$$\rho_0(\xi) = \psi^2(\xi, \eta = 0; R) = N(R) X^2(\xi) Y^2(0), \tag{34}$$

$N(R)$ being the normalisation function. Appendix B sets out the way the mirror plane density $\rho_0(\xi, R)$ can be calculated explicitly in practice. We turn therefore next to the H_2^+ ion in a magnetic field.

5.2. *H_2^+ in magnetic field along internuclear axis: some analytic results*

In this section we shall consider linear chains of protons, stabilised by a single electron plus a magnetic field of arbitrary strength $|\mathbf{B}| \equiv B$ along the internuclear axis. First, we give the theory for H_2^+ for arbitrary strength B. Then we deal with H_3^{2+} and H_4^{3+} in the limit of extremely strong fields, and summarise some available numerical results on the inhomogeneous electron densities for these two linear chains.

Returning to H_2^+, and employing units in which the electronic charge is -1, mass 1 and $\hbar = 1$, the Hamiltonian operator $\hat{H}$ takes the form [32]

$$\hat{H} = \frac{1}{2}(-i\nabla + \mathbf{A}/c)^2 + V, \tag{35}$$

where V is written for the potential energy and one has neglected the interaction between spin magnetic moment and the field.

For the constant magnetic field being considered, the vector potential $\mathbf{A}$ in Equation (35) is taken to have the form

$$\mathbf{A} = \frac{1}{2}\mathbf{B} \times \mathbf{r}. \tag{36}$$

The wave function ψ of the ground state is usefully written as a product of an electron density amplitude $\rho^{1/2}$ and a phase factor $\exp(i\theta)$.

What is important here is to introduce the current density $\mathbf{j}$, which can be written in the presence of the magnetic field as

$$\mathbf{j} = -\frac{i}{2}(\psi\nabla\psi^* - \psi^*\nabla\psi) - \frac{\mathbf{A}}{c}\psi\psi^* = \rho\nabla\theta + \frac{\mathbf{A}}{c}\rho. \tag{37}$$

Then one obtains for the ground-state energy $E^+(R, B)$ the result

$$E^+(R, B) = \frac{\hat{H}\psi}{\psi} = \frac{(\nabla\rho)^2}{8\rho^2} - \frac{\nabla^2\rho}{\rho} + \frac{j^2}{2\rho^2} + \frac{i\nabla \cdot \mathbf{j}}{2\rho} + V, \tag{38}$$

this Equation (38) being valid at any arbitrary position $\mathbf{r}$. For stationary wave functions, corresponding to time-independent electron density $\rho(R, B)$, the equation of continuity then yields the condition div $\mathbf{j} = 0$ to be satisfied by the current density vector $\mathbf{j}$. Hence, the result for the ground-state energy in Equation (38) becomes [32]

$$E^{+}(R, B) = \frac{(\nabla\rho)^2}{8\rho^2} - \frac{\nabla^2\rho}{4\rho} + \frac{j^2}{2\rho^2} + V, \tag{39}$$

which is the key result of this discussion of H_2^+ in a magnetic field of arbitrary strength B.

5.3. H_3^{2+} *and* H_4^{3+}*: linear configurations with B field along the axis: intense field limit*

Benguria *et al.* [33] have proposed a suitable limiting form of the exact Hamiltonian for such molecular ions which is appropriate in the limit of exceeding high magnetic fields $\mathbf{B}$ in linear configurations of ions such as H_3^{2+} and H_4^{3+}, stablised by applying the $\mathbf{B}$ field along the internuclear axis.

Amovilli and March [34] used the model Hamiltonian

$$\hat{H}_m = -\frac{1}{2}\frac{\partial^2}{\partial x^2} + \lambda\delta\left(x + \frac{b}{2}\right) + \lambda\delta\left(x - \frac{b}{2}\right) \tag{40}$$

to study the Feynman propagator of H_2^+ in an intense magnetic field along the x-axis, coinciding with the molecular axis. The two nuclei were sited at positions $-b/2$ and $b/2$, respectively. In Equation (40) lengths and energies are appropriately scaled.

Amovilli *et al.* [35] have subsequently studied the electron liquids created by a more general model potential $V(x)$ than that appearing in Equation (40), to be employed with n hydrogen nuclei in a linear configuration. Thus, following Equation (40)

$$V(x) = \lambda \sum_{j=1}^{n} \delta(x - a_j), \tag{41}$$

where $\lambda = -1$ and a_j denote the positions of the nuclei in atomic units and scaled by the factor L defined by

$$L(B) = 2W\left(\frac{\sqrt{B/B_0}}{2}\right). \tag{42}$$

In Equation (42) $W(z)$ is the Lambert function, B the strength of the magnetic field while $B_0 = 2.35 \times 10^9$ G. Fields exceeding by orders of magnitude this value of B_0 are indeed found at the surfaces of some neutron stars. The motion perpendicular to and along the field then become distinct from each other, as they involve energy scaling different by many orders of magnitude, as discussed in the review by Turbiner and Vieyra [36].

Amovilli and March [34] obtained the canonical density matrix $C(x, x', \beta)$ [37] for the high field limit of H_2^+. Their work can be generalised to a linear model of $H_n^{(n-1)+}$, yielding [35]

$$G(x, x', s) = \int_0^{\infty} \exp(-s\beta) C(x, x', \beta) \mathrm{d}\beta, \tag{43}$$

which is essentially the one-particle Green function evaluated at $E = -s$. For the linear chain described above, one finds [35]

$$G(x, x', s) = G_0(x - x', s) + \sum_{j=1}^{n} G_0(x - a_j, s) G(a_j, x', s). \tag{44}$$

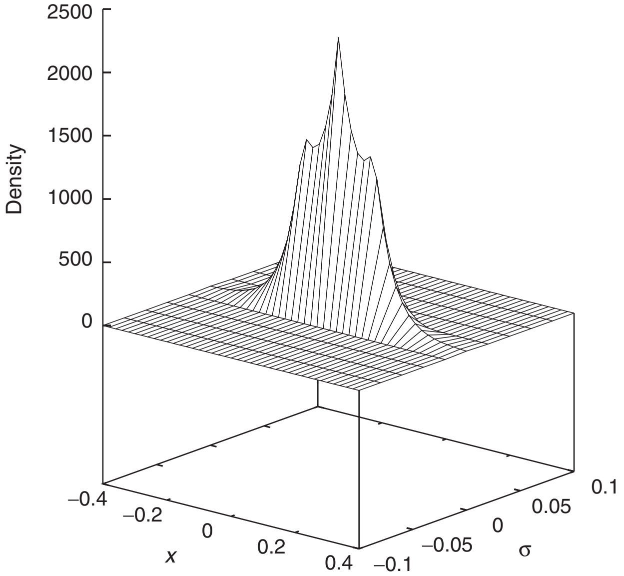


Figure 1. Depicts electronic probability density, in arbitary units for linear molecular ion H_3^{2+} in a **B** field of strength 4.4×10^{13} Gauss along internuclear axis. x denotes coordinates along molecular axis while σ measures distance from axis. Lengths are given in atomic units, and nuclei are at x coordinates −0.11, 0 and 0.11 (redrawn from [35]).

In Equation (43)

$$G_0(x - x', s) = \frac{1}{\sqrt{2s}} \exp\left(-\sqrt{2s}\,|x - x'|\right). \tag{45}$$

Using this procedure, the density of the inhomogeneous electron liquid can be calculated for both H_3^{2+} and H_4^{3+}, and the forms are displayed for a specified **B** field of strength ~10^{13} Gaussian parallel to the internuclear axis in Figures 1 and 2.

The above model can also be employed to calculate electronic transitions between bound states, as well as to obtain ground-state properties such as are displayed in Figures 1 and 2, but we shall not go into further details here.

6. Summary and future directions

Confinement of one electron in a bare Coulomb field has been treated in (a) one-centre cases in Section 2 and (b) in multicentre cases in Section 5, the application of an intense magnetic field along the linear chains of protons treated there stabilising H_3^{2+} and H_4^{3+}.

Then the effect of electron–electron repulsions on the electron liquids in Coulomb confined systems has been dealt with in some detail, Section 3 being concerned with two-electron He-like model atoms from first principles. Section 4 is different in two respects; namely, it deals with Be, Ne, Mg and Ar neutral atoms by non-relativistic quantum mechanics, but transcends HF theory by the semi-empirical insertion of ionisation potentials. Evidence is presented that this fine tuning of HF ground-state electron densities [27] is leading to results of QMC quality.

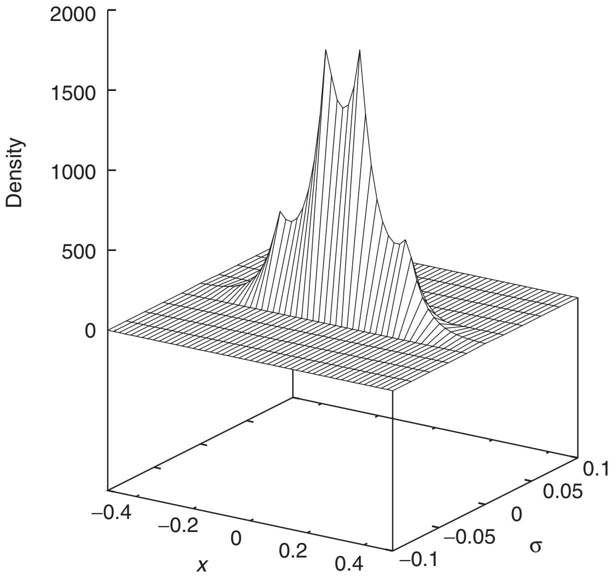


Figure 2. Similar to Figure 1 but now for linear ion H_4^{3+}: field strength again 4.4 × 10^{13} Gauss. x and σ as in Figure 1. Nuclei are now at x coordinates −0.225, −0.058, 0.058 and 0.225, measured in atomic units (redrawn from [35]).

As to future directions which should prove fruitful, the fine-tuning of HF densities should be extended to molecules and clusters. However, one problem that immediately arises is that the work of Cordero *et al.* [27] avoided the use of basis sets in treating light spherical atoms, by solving the HF equations numerically. To extend such a procedure to molecules, a natural starting point would be the 'almost spherical' cases like CH_4 and SiH_4, using a so-called 'one-centre' quantum chemical expansion. Finally, returning to bare Coulomb confinement, further attempts to find closed analytic solutions of equations like (19) for the Slater sum should, we believe, prove fruitful, giving further insight into the inhomogeneous electron liquids thereby created.

Acknowledgements

The writer acknowledges that this work, begun in the University of Antwerp (UA), was brought to fruition during a visit to ICTP, Trieste, Italy. Thanks are due to Professors D. Van Dyck and D. Lamoen for making possible the continuing affiliation of NHM with the UA. He was partially supported by UA through the BOF-NOI. At ICTP, Trieste, Professors V.E. Kravtsov and E. Tosatti are thanked both for generous hospitality and for the very stimulating environment in which this study was completed.

References

[1] I.A. Howard and N.H. March, Phys. Rev. A **69**, 044703 (2004).
[2] I.H. Duru and H. Kleinert, Fortschr. Phys. **30**, 401 (1982).
[3] P.M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953).
[4] N.H. March and L.M. Nieto, Phys. Chem. Liq. **45**, 295 (2007).

[5] N.H. March and A.M. Murray, Phys. Rev. **120**, 830 (Reprinted in Ref. [38]) (1960).
[6] T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957).
[7] N.H. March, Phys. Rev. A **33**, 88 (Reprinted in Ref. [38]) (1986).
[8] N.H. March, L.M. Nieto, C. Amovilli, L.C. Balbas, and M.L. Glasser, J. Math. Phys. **40**, 2671 (1999).
[9] I.L. Cooper, Phys. Rev. A **50**, 1040 (1994).
[10] S. Pfalzner, H. Lehmann, and N.H. March, J. Math. Chem. **16**, 9 (Reprinted in Ref. [38]) (1994).
[11] H. Lehmann and N.H. March, Phys. Chem. Liq. **27**, 65 (Reprinted in Ref. [38]) (1994).
[12] I.A. Howard and N.H. March, Phys. Stat. Sol. (b) **237**, 265 (Reprinted in Ref. [38]) (2003).
[13] I.A. Howard, F. Bartha, N.H. March, and A. Nagy, Phys. Lett. A **350**, 236 (2006).
[14] S. Chandrasekhar, Astrophys. J. **100**, 176 (1944).
[15] I.A. Howard and N.H. March, Phys. Lett. A **366**, 451 (2007).
[16] C. Amovilli, N.H. March, I.A. Howard, and A. Nagy, Phys. Lett. A **372**, 4053 (2008).
[17] M. Hoffmann-Ostenhof and T. Hoffmann-Ostenhof, Phys. Rev. A **16**, 1782 (1977).
[18] C. Schwartz, Ann. Phys. (NY) **6**, 156 (1959).
[19] N.H. March and R. Pucci, Phys. Lett. A **85**, 75 (1981).
[20] I.A. Howard and N.H. March, Phys. Rev. A **71**, 04250 (2005).
[21] A. Temkin, Phys. Rev. A **126**, 130 (1962).
[22] L.U. Ancarani, J. Phys. B: At. Mol. Opt. Phys. **39**, 3309 (2006).
[23] P. Serra, Phys. Rev. A **74**, 016501 (2006).
[24] C. Amovilli and N.H. March, Phys. Rev. A **72**, 042504 (2005).
[25] A. Nagy and C. Amovilli, J. Chem. Phys. **121**, 6640 (2004).
[26] A. Holas, I.A. Howard, and N.H. March, Phys. Lett. A **310**, 451 (2003).
[27] N.A. Cordero, N.H. March, and J.A. Alonso, Phys. Rev. A **79**, 052502 (2007).
[28] C. Møller and M.S. Plesset, Phys. Rev. **46**, 618 (1934).
[29] N.H. March, J.A. Alonso, and J.M. Lopez, Mol. Phys. **79**, 1143 (1993).
[30] O. Burrau, Det. Kgl. Danske Vid. Selgkab. **7**, 458 (1930).
[31] L. Pauling and E. Bright Wilson, *Introduction to Quantum Mechanics with Applications to Chemistry* (McGraw-Hill, New York, 1935).
[32] C. Amovilli and N.H. March, Chem. Phys. **146**, 207 (1990).
[33] R.D. Benguria, R. Brunmelhuis, P. Duclos, and S. Peréz-Oyarzún, J. Phys. B **37**, 2311 (2004).
[34] C. Amovilli and N.H. March, Int. J. Quant. Chem. **106**, 533 (2006).
[35] C. Amovilli, N.H. March, and P. Schmelcher, Phys. Lett. A **362**, 449 (2007).
[36] A.V. Turbiner and J.C.L. Vieyra, Phys. Rep. **424**, 309 (2006).
[37] N.H. March, W.H. Young, and S. Sampanthar, *The Many-Body Problem in Quantum Mechanics* (Dover, New York, 1995).
[38] N.H. March and G.G.N. Angilella, editors, *Many-body Theory of Molecules, Clusters, and Condensed Phases* (World Scientific, Singapore, 2009).
[39] A.K. Theophilou and N.H. March, Phys. Rev. A **34**, 3630 (1987).
[40] I.A. Howard, I.V. Komarov, N.H. March, and L.M. Nieto, J. Phys. A: Math. Gen. **36**, 4757 (2003).
[41] D. Layzer, Ann. Phys. **8**, 271 (1959).
[42] N.H. March and R.J. White, J. Phys. B **5**, 466, (Reprinted in Ref. [38]) (1972).
[43] E.A. Hylleraas, Z. Phys. **65**, 209 (1930).

Appendix A: Dirac density matrix for the *m*-th closed shell generated by a bare Coulomb field in terms of electron density

The purpose of this appendix is to record the use of the off-diagonal generalisation of the spatial form of Kato's theorem obtained by the writer for any arbitrary closed shell generated by the bare Coulomb potential. For convenience, we take $Z = 1$ and use atomic units throughout this appendix.

The Theophilou–March relation [39] reads

$$\gamma_m(\mathbf{r},\mathbf{r}') = -(x-y)^{-1}\left(\frac{\partial}{\partial x}-\frac{\partial}{\partial y}\right)\left(xy\gamma_{ms}\frac{x}{2},\frac{y}{2}\right), \tag{46}$$

where $x = r + r' + |\mathbf{r}-\mathbf{r}'|$ and $y = r + r' - |\mathbf{r}-\mathbf{r}'|$. The s-state matrix for the m-th closed shell can be written immediately in the factorised form

$$\gamma_{ms}(r,r') = n_{ms}^{1/2}(r)n_{ms}^{1/2}(r'), \tag{47}$$

where $n_{ms}(r)$ is the s-state density for the m-th closed shell. Hence in Equation (46) a key quantity appearing on the RHS is given explicitly by

$$xy\gamma_{ms}\left(\frac{x}{2},\frac{y}{2}\right) = xn_{ms}^{1/2}\left(\frac{x}{2}\right)yn_{ms}^{1/2}\left(\frac{y}{2}\right). \tag{48}$$

Then it is a purely mathematical matter to show, after some calculation, that the Dirac density matrix for the m-th closed shell is given by

$$\gamma_m(\mathbf{r},\mathbf{r}') = \gamma_{ms}\left(\frac{x}{2},\frac{y}{2}\right) - \frac{xy}{4(x-y)}\left[n_{ms}^{1/2}\left(\frac{y}{2}\right)n_{ms}^{-1/2}\left(\frac{x}{2}\right) - n_{ms}^{1/2}\left(\frac{x}{2}\right)n_{ms}^{-1/2}\left(\frac{y}{2}\right)n'_{ms}\left(\frac{y}{2}\right)\right]. \tag{49}$$

Employing explicit hydrogenic wavefunctions involving the generalised Laguerre polynomials one has

$$n_{ms}^{1/2}\left(\frac{x}{2}\right) = \frac{1}{\pi^{1/2}}m^{-5/2}\exp\left(-\frac{x}{2m}\right)\left[L_{m-1}^{(1)}\left(\frac{x}{m}\right)\right]. \tag{50}$$

Substituting Equation (50) into Equation (49) recovers an explicit result given by Howard *et al.* [40].

The additional merit of the form (49) is that it expresses the Dirac density matrix $\gamma_m(\mathbf{r},\mathbf{r}')$ for the entire m-th closed shell in terms of the s-state electron density only. Using the spatial generalisation of Kato's theorem given by the writer, one can relate $\gamma_m(\mathbf{r},\mathbf{r}')$ via Equation (49) solely to its diagonal density, i.e.

$$\gamma_m(\mathbf{r},\mathbf{r}') = \gamma_m[n_m]. \tag{51}$$

This is a central aim of current work on density matrix functional theory, and therefore this aim has been achieved, quite explicitly, for the hydrogenic limit of the $1/Z$ expansion of atomic theory [41,42].

Appendix B: Ground-state electron density of H_2^+ characterised by the mirror-plane density

As set out in Equation (32) of the main text, the ground-state wave function of H_2^+ in zero magnetic field is determined by the functions $X(\xi)$ and $Y(\eta)$ entering this equation. These functions are the physically significant solutions of the linear differential equations

$$\frac{\mathrm{d}}{\mathrm{d}\xi}\left(\left\{\xi^2-1\right\}\frac{\mathrm{d}X}{\mathrm{d}\xi}\right) + \left(-\lambda\xi^2 + 2D\xi + \mu\right)X = 0 \tag{52}$$

and

$$\frac{\mathrm{d}}{\mathrm{d}\eta}\left(\left\{1-\eta^2\right\}\frac{\mathrm{d}Y}{\mathrm{d}\eta}\right) + \left(-\lambda\eta^2 - \mu\right)Y = 0. \tag{53}$$

In Equations (52) and (53), λ measures the ground-state energy $E(R)$, $\mu = \mu(k)$ is a separation constant resulting from the substitution of Equation (32) in the Schrödinger equation, while D in Equation (52) is R in units of the Bohr radius a_0.

Fortunately, λ is known to high accuracy from the study of Hylleraas [43] and others as

$$\mu = \frac{1}{3}\lambda + \frac{2}{135}\lambda^2 + \frac{4}{8505}\lambda^3 - 0.000013\lambda^3 - 0.0000028\lambda^5 + \cdots. \tag{54}$$

Solving Equation (52), March *et al.* [29] plot $\rho_0(s/R_e)$ in Equation (34) in their figure, where s is the perpendicular distance from the bond axis and R_e is the equilibrium internuclear separation.

To complete the total ground-state electron density from the mirror plane density alone, the following steps are then to be taken: (i) Given the mirror plane density amplitude $X(\xi)$, and although the physical range of the independent variable is from 1 to ∞, Equation (52) allows the analytic continuation of $X(\xi)$: suppose that this is accomplished down to $\xi = -1$. (ii) Given (i), $Y(\eta)$ in Equation (53) can be determined next in the physical range from -1 to 1. (iii) Then $Y(\eta)$ in (ii) can be related to the analytic continuation of the mirror plane amplitude as follows. Viewing Y as $Y(\xi)$, one observes that $\mu - \lambda\xi^2$ is common between Equations (52) and (53). Eliminating this quantity between the two equations then leads to the result

$$\frac{1}{Y}\frac{\mathrm{d}}{\mathrm{d}\xi}\left((\xi^2 - 1)\frac{\mathrm{d}Y}{\mathrm{d}\xi}\right) = \frac{1}{X}\frac{\mathrm{d}}{\mathrm{d}\xi}\left(\{\xi^2 - 1\}\frac{\mathrm{d}X}{\mathrm{d}\xi}\right)2D\xi. \tag{55}$$

Equation (55) can now be viewed, for H_2^+, as the parallel relation to that between $\rho(r)$ and its s-state component only, $\rho_s(r)$, for the one-centre Coulomb problem. Inserting into the RHS the given analytic continuation of the mirror plane density amplitude $X(\xi)$, the integration of Equation (55), subject, of course, to the appropriate physical boundary conditions, suffices to determine $Y(\xi)$ in the physical range -1 to 1. This completes the calculation of the complete electron density $\rho(r)$ using the square of the wave function (32).