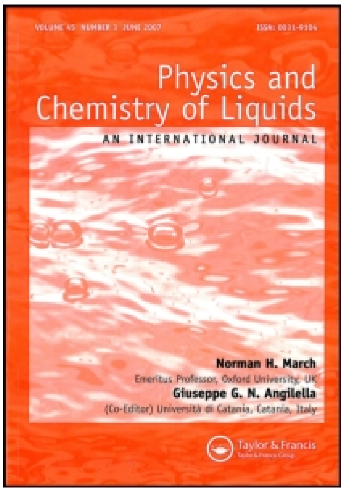

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INHOMOGENEOUS ELECTRON LIQUID: H ATOM DIRAC DENSITY MATRIX IN LIMIT OF INFINITE NUMBER OF CLOSED SHELLS

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The Dirac density matrix $\rho_{\mathcal{N}}(\vec{r},\vec{r}')$ for the H atom with $\mathcal{N}$ closed shells is here treated in the limit $\mathcal{N}$ tends to infinity. Then $\rho_{\infty}(\vec{r},\vec{r}')$is shown to be derivable exactly from the zero energy limit of the bound state only Green function $G_b^{(Z)}(\vec{r},\vec{r}';E)$. It is further demonstrated for nuclear charge Ze that the Laplace transform of $G_b^{(Z)}$ with respect to Z satisfies a useful equation of motion. Finally the s-wave only components of $\rho_{\mathcal{N}}$ and $G_b^{(Z)}$ are considered.

Keywords: Electron liquid; density matrix; bound-state Green function

1. BACKGROUND

Though, of course, many properties of the hydrogen-like atom are well established, fundamental quantities like the Feynman propagator are still not available in a compact, usable form. However, in the recent work of Blinder [1], an infinite series for this propagator has been established. The propagator, as Blinder stresses, is related to the canonical density matrix $C(\vec{r},\vec{r}',\beta)$ defined by

$$C(\vec{r},\vec{r}',\beta) = \sum_{\text{all}\, i} \psi_i(\vec{r})\psi_i^*(\vec{r}')\exp(-\beta\epsilon_i) \qquad : \beta = (k_B T)^{-1} \tag{1}$$

where the ψ_i's are the normalized eigenfunctions, with corresponding eigenvalues ε_i, of the hydrogenic Hamiltonian

$$\hat{H}_{\vec{r}} = -\frac{\hbar^2}{2m}\nabla_{\vec{r}}^2 - \frac{Ze^2}{r} \tag{2}$$

for nuclear charge Ze. The canonical density matrix C satisfies the Bloch equation

$$\hat{H}_{\vec{r}}C = -\frac{\partial C}{\partial \beta}, \tag{3}$$

to which we shall return below.

A parallel development has been concerned with the Dirac density matrix for the $\mathcal{N}$ closed shells $\rho_{\mathcal{N}}(\vec{r},\vec{r}')$, defined by

$$\rho_{\mathcal{N}}(\vec{r},\vec{r}') = \sum_{n=1}^{\mathcal{N}}\sum_{l=0}^{n-1}\sum_{m=-l}^{l} \psi_{nlm}(\vec{r})\psi_{nlm}^{*}(\vec{r}'). \tag{4}$$

March and Santamaria [2] demonstrated that for $\mathcal{N}=2(K+L$ shells), $\rho_2(\vec{r},\vec{r}')$ was the second-order polynomial $\rho(\frac{r_1+r_2}{2}) + f(\frac{r_1+r_2}{2})$ $|\vec{r}_1 - \vec{r}_2|^2$ in $|\vec{r}_1 - \vec{r}_2|$. Systematically higher-order polynomials result from continually adding further shells M, N etc. Here, prompted by the very recent study by Heilmann and Lieb [3, 4] (HL) on the diagonal electron density $\rho_\infty(r) = \rho_\infty(\vec{r},\vec{r}')_{\vec{r}'=\vec{r}}$ in the limit as the number of closed shells in equation (4) tends to infinity (see also Appendix 1 for the Fourier transform), we shall focus on the off-diagonal Dirac density matrix in this limit. As with ρ_2 discussed above, appropriate variables are $r+r'$ and $|\vec{r}-\vec{r}'|$, as follows, in fact, from the Runge-Lenz vector [5] as a constant of motion for the bare Coulomb Hamiltonian (2).

2. RELATION OF DIRAC DENSITY MATRIX $\rho_\infty(\vec{r},\vec{r}')$ TO BOUND-STATE GREEN FUNCTION

What we shall demonstrate below is an intimate connection between $\rho_\infty(\vec{r},\vec{r}')$ and a certain limit of the bound-state only Green function

$G_b^{(Z)}(\vec{r},\vec{r}\,';E)$, defined by

$$G_b^{(Z)}(\vec{r},\vec{r}\,';E) = \sum_{n=1}^{\infty}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}\frac{\psi_{nlm}(\vec{r})\psi^*_{nlm}(\vec{r}\,')}{E-\epsilon_n+i\eta} \tag{5}$$

where ϵ_n are the Coulomb bound levels $-Z^2e^2/2\,n^2a_0$, with a_0 the Bohr radius $\hbar^2/me^2$.

Let us immediately put $E=0$ in equation (5) to find

$$G_b^{(Z)}(\vec{r},\vec{r}\,';E=0) = \sum_{n=1}^{\infty}\sum_{l=0}^{n-1}\sum_{m=-l}^{l}\frac{\psi_{nlm}(\vec{r})\psi^*_{nlm}(\vec{r}\,')}{-\epsilon_n}. \tag{6}$$

The RHS can alternatively be constructed from the canonical or Bloch density matrix in equation (1), with the sum now restricted to the bound-states, as

$$\lim_{\beta\to 0}\int_{\beta}^{\infty} d\beta'\, C_b(\vec{r},\vec{r}\,',\beta') = -G_b^{(Z)}(\vec{r},\vec{r}\,';E=0). \tag{7}$$

Applying $\nabla^2_{\vec{r}}$, to equation (7) and using the Bloch equation (3) readily yields

$$\rho_\infty(\vec{r},\vec{r}\,') = \left[\frac{\hbar}{2m}\nabla^2_{\vec{r}}G_b^{(Z)}(\vec{r},\vec{r}\,';E) + \frac{Ze^2}{r}G_b^{(Z)}(\vec{r},\vec{r}\,';E)\right]_{E=0}. \tag{8}$$

This is a central result of the present study.

We turn immediately to discuss the form of the bound state Green function, which is evidently required to evaluate the limiting Dirac density matrix $\rho_\infty(\vec{r},\vec{r}\,')$ from equation (8). Fortunately, Van Hoang *et al.* [6, 7] have considered $G_b^{(Z)}$ for the hydrogenic atom by utilizing the well established correspondence with the isotropic harmonic oscillator in two-dimensional complex space.

Their result may be written, in atomic units ($e=1$, $\hbar=1$, $m=1$),

$$G_b^{(Z)}(\vec{r},\vec{r}\,';E) = -\frac{\omega}{2\pi}\int_0^{\infty} dt\exp\left(i\frac{2Z}{\omega}t\right)(\sin t)^{-2} \times\exp[i\omega(r+r')\cot t]J_0\left(\frac{\omega}{\sin t}\sqrt{2(rr'+\vec{r}\cdot\vec{r}\,')}\right) \tag{9}$$

where $\omega=\sqrt{-2E}$.

One can perform the $\nabla_{\vec{r}}^2$ operation entering equation (8) inside the integral and then write the formal limiting result

$$\rho_\infty(\vec{r},\vec{r}') = \lim_{E\to 0}\left\{\left[\frac{\hbar^2}{2m}\nabla_{\vec{r}}^2 G_b^{(Z)}\right] + \frac{Ze^2}{r} G_b^{(Z)}\right\}. \tag{10}$$

However, we must stress that while the result (10), using equation (9) is a complete solution for the Dirac density matrix, the order of the limiting process $E\to 0$ and the integration in equation (9) cannot be interchanged.

3. DIAGONAL EQUATION RELATING BOUND-STATE GREEN FUNCTION TO HL ELECTRON DENSITY

The starting point of this section is to define a function $S(r)$ from the diagonal part $G_b^{(Z)}(\vec{r},\vec{r}';E)$ of the bound-state Green function in the limit of zero energy, namely

$$S(r) = \lim_{\substack{\vec{r}\to\vec{r}' \\ E\to 0}} G_b^{(Z)}(\vec{r},\vec{r}';E). \tag{11}$$

The main aim in what follows is to derive a differential equation relating $S(r)$ to the HL electron density $\rho_\infty(r)$. Starting with off-diagonal information, use of the Schrödinger equation defined by the Coulomb Hamiltonian $\hat{H}_{\vec{r}}$ readily yields (compare equation (8))

$$\lim_{E\to 0} \hat{H}_{\vec{r}}\, G_b^{(Z)}(\vec{r},\vec{r}';E) = -\rho_\infty(\vec{r},\vec{r}') \tag{12}$$

where the RHS reduces to the HL density on the diagonal. Now one expands $G_b^{(Z)}(\vec{r},\vec{r}';E)$ above the diagonal $\vec{r}' = \vec{r}$, recognizing, following Blinder, that the appropriate variables are

$$x = r + r' + |\vec{r} - \vec{r}'| \tag{13}$$

and

$$y = r + r' - |\vec{r} - \vec{r}'|, \tag{14}$$

the Runge-Lenz vector being a constant of motion.

Then, after same manipulation, the desired result follows in the form

$$\frac{1}{8}S''' + \frac{1}{2r}S'' + \left(\frac{1}{4r^2} + \frac{Z}{r}\right)S' + \frac{Z}{2r^2}S = \rho'_\infty. \tag{15}$$

3.1. Solution for $S(r)$ at large r

HL give the large r form of $\rho_\infty(r)$, leading to (with $Z = 1$)

$$\rho'_\infty(r) = -\frac{3}{2}\frac{A}{r^{5/2}} \qquad : A = \frac{\sqrt{2}}{3\pi^2}. \tag{16}$$

Neglecting in the first instance the second and third derivatives at large r (a procedure to be confirmed below) and dropping the $1/4r^2$ term relative to Z/r, one has the first-order differential equation for $S(r)$, also putting $Z = 1$,

$$\frac{1}{r}S' + \frac{1}{2r^2}S = -\frac{3}{2}\frac{A}{r^{5/2}}. \tag{17}$$

It is readily verified that the solution is

$$S(r) = -\frac{3A\ln r}{2r^{1/2}} \qquad : r \to \infty. \tag{18}$$

This result demonstrates the pronounced non- analytic behaviour of the bound-state Green function $G_b^{(Z)}(\vec{r}, \vec{r}'; E)$ in the limits $E \to 0$ and $r \to \infty$.

We also remark at this point that although, as demonstrated by HL, $\rho_\infty(r)$ is finite as $r \to 0$, the presence of the eigenvalues $-Z^2/2n^2$ in the denominator of $G_b^{(Z)}(\vec{r}, \vec{r}'; E \to 0)$ leads to the divergence of $S(r)$ at the atomic nucleus.

Returning briefly to the off-diagonal form $G_b^{(Z)}(\vec{r}, \vec{r}'; E)$, and particularly its integral form (9), the simplicity of the Z dependence has prompted us to define the Laplace transform of $G_b^{(Z)}$ with respect to Z. We show in Appendix 2 that the resulting quantity satisfies a relatively simple equation of motion which may be valuable for future work in this area.

4. s-STATE COMPONENT OF $G_b^{(Z)}$ AND $\rho_\infty(\vec{r},\vec{r}')$

It is of interest to extract the s-wave component of $G_b^{(Z)}$ by integration over angles, using orthogonality of the Legendre polynomials. Then the result can be expressed directly in terms of the integral $I(x)$ defined by

$$I(x) = \int_0^x qJ_0(q)dq \tag{19}$$

which gives the s-component $G_{bs}^{(Z)}$ of $G_b^{(Z)}$ in the form

$$\begin{aligned} G_{bs}^{(Z)} = &-\frac{1}{2\pi\omega rr'}\int_0^\infty dt \exp\left(i\frac{2Z}{\omega}t\right) \\ &\times \exp[i\omega(r+r')\cot t] I\left(\frac{2\omega\sqrt{rr'}}{\sin t}\right). \end{aligned} \tag{20}$$

As for $\rho_\infty(\vec{r},\vec{r}')$, $\rho_{\infty s}(\vec{r},\vec{r}')$ can be obtained by allowing the Hamiltonian to act on $G_{bs}^{(Z)}$ in the limit $\omega \to 0$. The resulting equation in this case is

$$\rho_{\infty s}(\vec{r},\vec{r}') = \left[\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}G_{bs}^{(Z)} + \frac{2}{r}\frac{\partial}{\partial r}G_{bs}^{(Z)}\right) + \frac{Ze^2}{r}G_{bs}^{(Z)}\right]_{\omega=0}. \tag{21}$$

It is important to remark that the full Dirac density matrix $\rho_\infty(\vec{r},\vec{r}')$ is related to its s-wave component $\rho_{\infty s}(\vec{r},\vec{r}')$ by the Theophilou and March result [8]

$$\rho_\infty(\vec{r},\vec{r}') = \frac{1}{x-y}\left(\frac{\partial}{\partial x} - \frac{\partial}{\partial y}\right)\left[x\, y \rho_{\infty s}\left(\frac{x}{2},\frac{y}{2}\right)\right] \tag{22}$$

where x and y are the Blinder variables defined in (13) and (14).

5. SUMMARY AND DISCUSSION

The main results of this paper are (i) equation (8) relating the Dirac density matrix for hydrogen in the limit of an infinite number of closed shells to the bound-state Green function in the zero energy limit, (ii) the analogous result (21) for s-state and (iii) the large r limit of $S(r)$, the diagonal element of the bound-state Green function as $E \to 0$, in equation (18).

In future work, we expect the first integral representation of Heilmann and Lieb [3] for the density $\rho_\infty(\vec{r}, \vec{r})$ to relate to $\rho_\infty(\vec{r}, \vec{r}')$ through the idempotency condition

$$\rho_\infty(\vec{r}, \vec{r}) = \int |\rho_\infty(\vec{r}, \vec{r}')|^2 d\vec{r}'. \tag{23}$$

Evidently therefore, this integral representation contains some, albeit limited, information on the coordinate dependence of the off-diagonal Dirac density matrix.

Finally, the kinetic energy density $t_\infty(r)$, and its s-state only component $t_{\infty s}(r)$, can be calculated from $(\hbar^2/2m)\vec{\nabla}_{\vec{r}} \cdot \vec{\nabla}_{\vec{r}'} \rho_\infty(\vec{r}, \vec{r}')$. However, elsewhere we have shown [9] how kinetic energy densities can be expressed in terms of $\rho_\infty(r)$ and $\rho_{\infty s}(r)$, plus the Coulomb potential.

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APPENDIX 1.

X-ray factor $f_\infty(k)$ corresponding to density $\rho_\infty(r)$

The atomic scattering factor $f_\infty(k)$ is defined for an electron density distribution $\rho_\infty(r)$ as

$$f_\infty(k) = \int \rho_\infty(r)\exp(i\vec{k}\cdot\vec{r})d\vec{r}. \tag{A.1}$$

Utilizing the diagonal form of equation (8) and inserting into equation (A.1) gives, with Van Hoang *et al.* [6] result for $G_b^{(Z)}$ an explicit integral form for $f_\infty(k)$.

One can now examine the singularities of $f_\infty(k)$. The first result to focus on is the divergence at small k because of the HL asymptotic decay as $r^{-3/2}$ at large r.

Scaling after inserting this asymptotic form for $\rho_\infty(r)$ in equation (A.1) shows, with an appropriate small r cutoff that $f_\infty(k)$ scales as

$$f_\infty(k) \propto \int \frac{1}{r^{3/2}}\frac{\sin kr}{kr}4\pi r^2 dr. \tag{A.2}$$

Putting $kr = s$, one has

$$f_\infty(k) \propto \frac{1}{k^{3/2}} \tag{A.3}$$

the coefficient being determined by the HL constant A.

There are other singularities (non-analyticities) in $f_\infty(k)$ away from $k = 0$ and these lead to factors like sin $(r^{1/2})$ and $\cos(r^{1/2})$ appearing in the HL asymptotic expansion for $\rho_\infty(r)$.

APPENDIX 2.

Laplace transform of bound-state Green function with respect to nuclear charge

It is of interest to record in this Appendix that a potentially useful tool for future work is obtained by treating the nuclear charge Ze in the

Hamiltonian (2) as a continuous variable and taking the Laplace transform of $G_b^{(Z)}$, the bound-state Green function, with respect to Z. One then obtains the quantity

$$\tilde{K}_b(\vec{r},\vec{r}';\gamma,E)=\int_0^\infty \exp(-\gamma Z)G_b^{(Z)}(\vec{r},\vec{r}';E)dZ. \qquad (A.4)$$

From the 'equation of motion'

$$\nabla_{\vec{r}}^2 G_b^{(Z)}-\nabla_{\vec{r}'}^2 G_b^{(Z)}=\frac{2m}{\hbar^2}\left(-\frac{Ze^2}{r}+\frac{Ze^2}{r'}\right)G_b^{(Z)} \qquad (A.5)$$

it easy to show, by forming $\partial\tilde{K}_b/\partial\gamma$ from equation (A.4) to deal with the product $ZG_b^{(Z)}$ on the RHS of equation (A.5), that $\tilde{K}_b$ satisfies

$$\nabla_{\vec{r}}^2\tilde{K}_b-\nabla_{\vec{r}'}^2\tilde{K}_b=\frac{2}{a_0}\left(\frac{1}{r}-\frac{1}{r'}\right)\frac{\partial\tilde{K}_b}{\partial\gamma} \qquad (A.6)$$

As a modest example, let us extract simply the lowest bound-state contribution to $G_b^{(Z)}(\vec{r},\vec{r}';E)$ in the limit $E\to 0$ as

$$G_{b(1s)}^{(Z)}(\vec{r},\vec{r}';E=0)=\frac{2Z}{\pi a_0^3 e^2}\exp\left\{-\frac{Z}{a_0}(r+r')\right\}. \qquad (A.7)$$

Taking the Laplace transform according to equation (A.7) yields

$$\tilde{K}_{1s}(\vec{r},\vec{r}';\gamma,E=0)\propto\frac{1}{(\gamma+\frac{r+r'}{a_0})^2} \qquad (A.8)$$

which shows in this simple case that, for finite γ, $\tilde{K}_{1s}$ decays at large r and r' as $(r+r')^{-2}$.

Finally, the complete expression for $\tilde{K}_b$ is, inserting $G_b^{(Z)}$ from equation (9) into equation (A.5),

$$\tilde{K}_b(\vec{r},\vec{r}';\gamma,E)=-\frac{\omega}{2\pi}\int_0^\infty dt\frac{(\sin t)^{-2}}{(\gamma-i2t/\omega)}$$
$$\times\exp[i\omega(r+r')\cot t]J_0\left(\frac{\omega}{\sin t}\sqrt{2(rr'+\vec{r}\cdot\vec{r}')}\right) \qquad (A.9)$$

where a pole on the imaginary axis of t, in the function inside the integral, appears at the value $-i\gamma\omega/2$.