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Curvature of the total electron density at critical coupling: attractive impurity in an electron gas

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Abstract. Structural properties of the spherically averaged total charge density $\rho_\lambda(r)$ of a degenerate free electron gas distorted by the action of an attractive, screened potential $\lambda V(r)$ are studied. The total charge density is described as the sum over the occupied bound and scattering states of independent electrons moving in an effective central field. Each of the individual (bound, scattering) terms in the density presents discontinuities at threshold values of λ for which new bound states appear. Nevertheless, it is mathematically proven that these discontinuities cancel each other and that the density $\rho_\lambda(0)$ at the origin, as well as its two radial derivatives $\rho'_\lambda(0)$ and $\rho''_\lambda(0)$, are differentiable functions of λ for any $\lambda \geqslant 0$. The smooth behaviour implies that the curvature $\rho''_\lambda(0)$ at the origin does not provide a criterion for the bound-to-free transition in metallic environments.

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Contents

1. Introduction and motivations

Screening is a fundamental property of metallic electron gases [1]. When an external charge is embedded into an electron gas, electrons redistribute themselves so as to completely shield the charge at large distances. Screening reduces significantly the interaction range between charged particles and enhances locality in many processes. The understanding of how screening works in different situations [2]–[10] is basic to interpreting the output of many experimental techniques used in the structural characterization and spectroscopical analysis of materials.

Mean field is one of the most useful approximations to deal with the screening problem. In mean field theory, one replaces the many-body Schrödinger equation by a single-particle Schrödinger equation. The many-body effects come via the single-particle potential $\lambda V(r)$ which can be generated, in a self-consistent picture, from the particles themselves. If, in order to respect the Pauli exclusion principle for fermions, the many-body wavefunction is represented by a single determinant, then the one-particle density matrix $\hat{\rho}(\mathbf{r}, \mathbf{r}')$ is idem potent ($\hat{\rho} = \hat{\rho}^2$) and reduces to summation over occupied orbitals $\psi_n(\mathbf{r})$. The electronic density is then simply given by $\hat{\rho}(\mathbf{r}, \mathbf{r})$. In this independent-particle model the occupation numbers are fixed to be strictly zero or one for each spin, depending on whether the state in question is empty or filled [11]. For a charge embedded in an electron gas, and for a given density of the screening environment n_0, the total electronic density $\rho(\mathbf{r})$ is then obtained as a sum over occupied scattering eigenstates $\rho_{\mathrm{sc}}(\mathbf{r})$ plus a sum over bound states $\rho_{\mathrm{bd}}(\mathbf{r})$, if any:

$$\rho(\mathbf{r}) = \rho_{\mathrm{bd}}(\mathbf{r}) + \rho_{\mathrm{sc}}(\mathbf{r}). \tag{1}$$

Theoretical information on the structural properties of the density $\rho(\mathbf{r})$ is important in many aspects of physics and chemistry, and has been a matter of study from many different points of view. Motivated by the convergence problem of the Born-series expansion in scattering theory for a screened potential $\lambda V(r)$, the smooth character of the scattering solutions was already studied as a function of the potential strength λ in [12]. By means of a Hartree self-consistent field calculation, March and Murray investigated the screening

of a single positive charge and pointed out that the density at the impurity position $\rho(0)$ does not show any marked change due to the formation of a bound state [13]. Butler, and later Peierls, investigated the possibility of discontinuity in the physical variable $\rho(0) = \rho_{\rm bd}(0) + \rho_{\rm sc}(0)$ when a new bound state is created in the screened field of an impurity in an electron gas [14, 15]. By using Jost functions in the analysis, Butler and Peierls found a smooth behaviour of the total $\rho(0)$ at critical coupling. The smooth behaviour of $\rho(0)$ was demonstrated recently as well, in a comparative study on application of implicit and explicit functionals of density functional theory (DFT), by an analytical calculation [16] based on the prototype Hulthén potential [17, 18]. The dependence of the single-particle density matrix has been also analysed as a function of the coupling constant λ of a finite-range potential $\lambda V(r)$ for a fixed number of particles in the system by Kohn and Majumdar [19]. A general result on its analyticity was thereby shown. Our study can be considered as a nontrivial extension of that of Kohn and Majumdar [19], in which particular attention is paid to the contribution of the various partial-wave channels to the electronic density.

The main goal of this study is to provide a rigorous and extended analysis of the behaviour of the electronic density $\rho_\lambda(\mathbf{r})$ of a degenerate electron gas distorted by the action of a spherical potential $\lambda V(r)$ at the origin $r = 0$, and as a function of the potential coupling constant λ. We explicitly discuss the role of different angular-momentum channels by means of Jost functions. In particular, we will focus on the properties of the second radial derivative $\rho''_\lambda(r)$. We will show, in a unified manner, that $\rho_\lambda(0)$, $\rho'_\lambda(0)$, and $\rho''_\lambda(0)$ are differentiable functions of λ for any $\lambda > 0$. There are no discontinuities in λ that could be used as imprint for the appearance of bound states in an extended electron gas. A brief account of these results was published in [20].

The paper is organized as follows. Section 2 introduces the notation and proves the curvature theorem, which is the main result of this contribution. Section 3 includes numerical results that illustrate the applicability of the theorem to several examples. Section 4 is devoted to the particular case of the Coulomb potential, which has to be treated separately. Finally, a summary and the conclusions appear in section 5. Atomic units are used in the following unless otherwise stated.

2. Theorem of curvature

We start from a 3D degenerate electron gas in a central potential λV of strength λ. The ground state of this system is

$$|\Psi\rangle = \prod_n a_n^\dagger |0\rangle, \tag{2}$$

where $a_n^\dagger$ stands for the creation operator of a particle in state ψ_n, and the product runs over a convenient orthonormal basis of eigenstates ψ_n of

$$H_\lambda = -\tfrac{1}{2}\Delta + \lambda V \tag{3}$$

for all energies up to the Fermi level $E_{\rm F}$. In other words, $\{\psi_n\}$ is a basis of the one-electron Hilbert subspace $P_{H_\lambda \leqslant E_{\rm F}}\mathcal{H}$, where $P_{H_\lambda \leqslant E_{\rm F}}$ is the orthogonal projector on the subspace spanned by the eigenstates of H_λ with energy up to the Fermi level.

The physical charge density at $\mathbf{r}$ is given by

$$\rho(\mathbf{r}) = \langle\Psi|a^\dagger(\mathbf{r})a(\mathbf{r})|\Psi\rangle, \tag{4}$$

thus one has, in units of the electron charge, the usual form

$$\rho(\mathbf{r}) = \sum_n |\psi_n(\mathbf{r})|^2. \tag{5}$$

Our aim is to discuss the angular average $\rho_\lambda(r)$ of the electronic density $\rho(\mathbf{r})$:

$$\rho_\lambda(r) = \frac{1}{4\pi}\int_{S^2} \rho(\mathbf{r})\, \mathrm{d}\Omega_\mathbf{r}, \tag{6}$$

and its behaviour as a function of the coupling constant λ.

Let the expansion of an arbitrary regular wavefunction $\psi(\mathbf{r})$ in partial waves and in powers of r:

$$\psi(\mathbf{r}) = \sum_{LM} \psi_{LM}(\mathbf{r}) = \sum_{LM} R_{LM}(r) Y_L^M(\Omega_\mathbf{r}), \tag{7}$$

with

$$R_{LM}(r) = \sum_{s \geqslant L} c_{LMs} r^s. \tag{8}$$

The angular average of the density $|\psi|^2$ is defined as

$$g_\psi(r) = \frac{1}{4\pi}\int_{S^2} |\psi(\mathbf{r})|^2\, \mathrm{d}\Omega_\mathbf{r} = \frac{1}{4\pi}\sum_{LM} |R_{LM}(r)|^2 = \sum_{LM} g_{\psi_{LM}}(r). \tag{9}$$

Consequently, different partial waves contribute independently to $g_\psi(r)$, with no interference among them. In particular, $g_\psi(r)$ is insensitive to their relative phases.

Let the Taylor expansion of $g_\psi(r)$ around the origin:

$$g_\psi(r) = \sum_{n=0}^{\infty} \frac{1}{n!} g_\psi^{(n)}(0) r^n. \tag{10}$$

The regularity condition of the radial wavefunctions (see equation (8)) implies that L-waves do not contribute to $g_\psi^{(n)}(0)$, $\forall n < 2L$. In particular, only $L = 0$ waves contribute to $g_\psi(0)$, $g'_\psi(0)$, whereas only waves with $L = 0, 1$ contribute to $g''_\psi(0)$.

If $g_\psi(0) > 0$, define the ratios

$$\kappa_n(\psi) = \frac{g_\psi^{(n)}(0)}{g_\psi(0)}. \tag{11}$$

The regularity condition implies that L-waves do not contribute to κ_n, $\forall n < 2L$. The first important quantity, the cusp of ψ at the origin, is defined as

$$\mathrm{Cusp}_\psi(0) = \kappa_1(\psi) = \frac{g'_\psi(0)}{g_\psi(0)} = 2\mathrm{Re}(c_{001}/c_{000}) \tag{12}$$

Only $L = 0$ waves contribute to Cusp. The second important quantity, the curvature of ψ at the origin, is defined accordingly as

$$\mathrm{Curv}_\psi(0) = \kappa_2(\psi) = \frac{g''_\psi(0)}{g_\psi(0)} = 2\left[|c_{001}/c_{000}|^2 + 2\mathrm{Re}(c_{002}/c_{000}) + \sum_{|M|\leqslant 1} |c_{1M1}/c_{000}|^2\right]$$
$$\geqslant 2[|c_{001}/c_{000}|^2 + 2\mathrm{Re}(c_{002}/c_{000})]. \tag{13}$$

Only waves with $L = 0, 1$ contribute to Curv.

In the following, we will consider a central attractive potential $\lambda V(r)$ of finite range and strength $\lambda > 0$. $V(r)$ has the following series expansion around the origin:

$$V(r) = \frac{v_{-1}}{r} + \sum_{j=0}^{\infty} v_j r^j, \quad v_{-1} \leqslant 0. \tag{14}$$

In the screening problem of an external point charge Z embedded in a polarizable medium, one finds $Z = \lambda v_{-1}$ for the first term of this expansion. The next term in the expansion $\lambda v_0 = Z(v_0/v_{-1})$ describes the short-range deviation from the bare Coulomb potential. In section 3 of this study, a simple parametric form for $\lambda V(r)$ is used for illustrative purposes. In such one-parameter representation of the shielding potential, the v_j coefficients are simple. The particular case of the Coulomb potential requires a separate analysis that will be presented in section 4.

Let $\rho_{\lambda,\mathrm{bd}}(r)$ and $\rho_{\lambda,\mathrm{sc},E_\mathrm{F}}(r)$ denote the contribution to the angular average of the electron density due to bound and unbound electrons, respectively, and thus $\rho_{\lambda,E_\mathrm{F}}(r) = \rho_{\lambda,\mathrm{bd}}(r) + \rho_{\lambda,\mathrm{sc},E_\mathrm{F}}(r)$ is the total density. We intend to show that the charge density $\rho_{\lambda,E_\mathrm{F}}(r)$ is a smooth function of the coupling constant λ at least for r close to 0. More precisely, we will prove that the density $\rho_{\lambda,E_\mathrm{F}}(0)$ at the origin and its two radial derivatives $\rho'_{\lambda,E_\mathrm{F}}(0)$ and $\rho''_{\lambda,E_\mathrm{F}}(0)$, are differentiable functions of λ for any $\lambda \geqslant 0$. For this purpose, let us first analyse separately each of the two terms.

2.1. Bound states

Let a square-integrable wavefunction

$$\psi_{\lambda,LM,E}(\mathbf{r}) = r^{-1}u_{\lambda,L,E}(r)Y_L^M(\Omega_\mathbf{r}), \tag{15}$$

where $E(\leqslant 0) \in \sigma_\mathrm{p}(H_\lambda = -\frac{1}{2}\Delta + \lambda V)$, the point spectrum of H_λ. Such wavefunction is a regular solution of the Schrödinger equation

$$-\tfrac{1}{2}\Delta\psi_{\lambda,LM,E}(\mathbf{r}) + (\lambda V(r) - E)\psi_{\lambda,LM,E}(\mathbf{r}) = 0 \tag{16}$$

in the L, M channel. We shall assume that $||\psi_{\lambda,LM,E}|| = 1$. The energy operator in the subspace of eigenvectors of $\mathbf{L}^2$ with eigenvalue $L(L+1)$ will be denoted by $H_{\lambda,L}$. The spectrum of this operator has uniform multiplicity $2L + 1$. The reduced radial wavefunction $u_{\lambda,L,E}(r)$ is a regular

solution of the reduced radial equation for L-waves

$$-\tfrac{1}{2}u''(r) + [\lambda V(r) + L(L+1)/2r^2 - E]u(r) = 0 \tag{17}$$

such that

$$u_{\lambda,L,E}(r) \sim \alpha_{\lambda,L,E} r^{L+1} \text{asr} \to 0, \tag{18}$$

where $\alpha_{\lambda,L,E}$ is a normalization constant.

It is easy to see from equations (14) and (17) that

$$u_{\lambda,L,E}(r) = \alpha_{\lambda,L,E} r^{L+1}\left[1 + \frac{\lambda v_{-1}}{L+1}r + \frac{\lambda^2 v_{-1}^2 + (L+1)(\lambda v_0 - E)}{(L+1)(2L+3)}r^2 + \cdots\right]. \tag{19}$$

Therefore, we have

$$g_{\psi_{\lambda,LM,E}}(r) = \frac{1}{4\pi}\alpha_{\lambda,L,E}^2 r^{2L}\left[1 + 2\frac{\lambda v_{-1}}{L+1}r + \frac{(4L+5)\lambda^2 v_{-1}^2 + 2(L+1)^2(\lambda v_0 - E)}{(L+1)^2(2L+3)}r^2 + \cdots\right]. \tag{20}$$

Hence

$$\begin{aligned}
&g_{\psi_{\lambda,0,0,E}}(0) = \tfrac{1}{4\pi}|\alpha_{\lambda,0,E}|^2, \quad g_{\psi_{\lambda,LM,E}}(0) = 0 \quad \text{if } L \geqslant 1,\\
&\text{Cusp}_{\psi_{\lambda,0,0,E}}(0) = 2\lambda v_{-1}, \quad g'_{\psi_{\lambda,LM,E}}(0) = 0 \quad \text{if } L \geqslant 1,\\
&\text{Curv}_{\psi_{\lambda,0,0,E}}(0) = \tfrac{2}{3}[5\lambda^2 v_{-1}^2 + 2(\lambda v_0 - E)],\\
&g''_{\psi_{\lambda,1,M,E}}(0) = 3 \times \tfrac{1}{4\pi}2|\alpha_{\lambda,1,E}|^2, \quad g''_{\psi_{\lambda,LM,E}}(0) = 0 \quad \text{if } L \geqslant 2.
\end{aligned} \tag{21}$$

It is clear that

$$\rho_{\lambda,\text{bd}}(r) = \sum_{L,E\in\sigma_\text{p}(H_{\lambda,L})} \rho_{\lambda,L,E}(r) = 2 \times \sum_{LM,E\in\sigma_\text{p}(H_{\lambda,L})} g_{\psi_{\lambda,LM,E}}(r), \tag{22}$$

where $\rho_{\lambda,L,E}(r)$ represents the contribution of the $2(2L+1)$ electrons filling the bound orbitals with quantum numbers L, E:

$$\begin{aligned}
\rho_{\lambda,L,E}(r) = 2 \times (2L+1) \times \frac{1}{4\pi}|u_{\lambda,L,E}|^2 &= \frac{2L+1}{2\pi}|\alpha_{\lambda,L,E}|^2 r^{2L}\\
&\times\left[1 + 2\frac{\lambda v_{-1}}{L+1}r + \frac{(4L+5)\lambda^2 v_{-1}^2 + 2(L+1)^2(\lambda v_0 - E)}{(L+1)^2(2L+3)}r^2 + \cdots\right].
\end{aligned} \tag{23}$$

It is evident that only those terms with $L = 0$ contribute to $\rho_{\lambda,\mathrm{bd}}(0)$, $\rho'_{\lambda,\mathrm{bd}}(0)$, whereas only $L = 0, 1$ terms need be considered for $\rho''_{\lambda,}(0)$:

$$\begin{aligned}
\rho_{\lambda,\mathrm{bd}}(0) &= \sum_{E\in\sigma_{\mathrm{p}}(H_{\lambda,0})} \rho_{\lambda,0,E}(0) = 2\times\frac{1}{4\pi}\sum_{E\in\sigma_{\mathrm{p}}(H_{\lambda,0})}|\alpha_{\lambda,0,E}|^2,\\
\rho'_{\lambda,\mathrm{bd}}(0) &= \sum_{E\in\sigma_{\mathrm{p}}(H_{\lambda,0})} \rho'_{\lambda,0,E}(0) = 2\lambda v_{-1}\rho_{\lambda,\mathrm{bd}}(0),\\
\rho''_{\lambda,\mathrm{bd}}(0) &= \sum_{0\leqslant L\leqslant 1, E\in\sigma_{\mathrm{p}}(H_{\lambda,L})} \rho''_{\lambda,L,E}(0)\\
&= \sum_{E\in\sigma_{\mathrm{p}}(H_{\lambda,0})}\frac{1}{3\pi}[5\lambda^2 v_{-1}^2 + 2(\lambda v_0 - E)]|\alpha_{\lambda,0,E}|^2 + \frac{3}{\pi}\sum_{E\in\sigma_{\mathrm{p}}(H_{\lambda,1})}|\alpha_{\lambda,1,E}|^2.
\end{aligned} \tag{24}$$

When the coupling constant increases and crosses a threshold $\lambda_{L,n}$, $n = 1, 2, \ldots$, for appearance of an nth bound state in the sector of angular momentum L, the quantities $\rho_{\lambda,\mathrm{bd}}(0)$, $\rho'_{\lambda,\mathrm{bd}}(0)$, $\rho''_{\lambda,\mathrm{bd}}(0)$ show the following typical behaviours: $\rho_{\lambda,\mathrm{bd}}(0)$, $\rho'_{\lambda,\mathrm{bd}}(0)$ present cusps at the thresholds $\lambda_{0,n}$, while $\rho''_{\lambda,\mathrm{bd}}(0)$ has finite discontinuities. This has a simple explanation: in s-waves there is no zero-energy bound state, and the amplitude $\alpha_{\lambda,0,n} = 0$ at threshold, while for $L \geqslant 1$ waves there are zero-energy bound states at the critical values of the coupling strength and thus the normalizing amplitudes $\alpha_{\lambda,L,n} \neq 0$.

2.2. Scattering states

A wavefunction $\psi^+_{\lambda,\mathbf{k}}(\mathbf{r})$, $E = k^2/2 \geqslant 0$, which is an outgoing scattering state with incoming momentum $\mathbf{k}$ and normalized to the $\mathbf{k}$-scale:

$$\langle\psi^+_{\lambda,\mathbf{k}'}|\psi^+_{\lambda,\mathbf{k}}\rangle = \delta(\mathbf{k}' - \mathbf{k}). \tag{25}$$

The partial wave expansion of $\psi^+_{\lambda,\mathbf{k}}(\mathbf{x})$ can be written as

$$\begin{aligned}
\psi^+_{\lambda,\mathbf{k}}(\mathbf{r}) &= (2/\pi)^{1/2}\sum_{LM}\mathrm{i}^L\frac{u^+_{\lambda,L,k}(r)}{kr}Y_L^M(\Omega_{\mathbf{r}})Y_L^{M*}(\Omega_{\mathbf{k}})\\
&= (1/2\pi^3)^{1/2}\sum_{L}\mathrm{i}^L\left(L+\frac{1}{2}\right)\frac{u^+_{\lambda,L,k}(r)}{kr}P_L(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}).
\end{aligned} \tag{26}$$

Therefore, in this case

$$R_{\lambda,LM,k}(r) = (2/\pi)^{1/2}\mathrm{i}^{\mathrm{L}}\frac{\mathrm{u}^+_{\lambda,\mathrm{L},\mathrm{k}}(\mathrm{r})}{\mathrm{kr}}\mathrm{Y}_{\mathrm{L}}^{\mathrm{M}*}(\Omega_{\mathbf{k}}). \tag{27}$$

The reduced radial function $u^+_{\lambda,L,k}(r)$ is the regular solution of the equation

$$-\tfrac{1}{2}u''(r) + [\lambda V(r) + \tfrac{1}{2}L(L+1)r^{-2} - \tfrac{1}{2}k^2]u(r) = 0 \tag{28}$$

with asymptotic behaviour at large distances

$$u^{+}_{\lambda,L,k}(r) \underset{r\to\infty}{\sim} \mathrm{e}^{\mathrm{i}\delta_{\lambda,\mathrm{L}}(k)} \sin\left[kr - \tfrac{1}{2}L\pi + \delta_{\lambda,L}(k)\right], \tag{29}$$

where $\delta_{\lambda,L}(k)$ is the L-wave phase shift for momentum k.

It is known that if $F_{\lambda,L}(k)$ is the Jost function in the L-channel, given by [21]–[23]

$$F_{\lambda,L}(k) = 1 + \frac{2\mathrm{i}}{k}\lambda \int_0^\infty \mathrm{d}r \tilde{h}^{(1)}_L(kr) V(r) v_{\lambda,L,k}(r), \tag{30}$$

where $\tilde{h}^{(1)}_L(z) = \tilde{j}_L(z) + \mathrm{i}\,\tilde{y}_L(z)$, and $\tilde{f}(z) = zf(z)$, then

$$u^{+}_{\lambda,L,k}(r) = F^{-1}_{\lambda,L}(k) v_{\lambda,L,k}(r), \tag{31}$$

where

$$v_{\lambda,L,k}(r) \underset{r\to 0}{\sim} [(2L+1)!!]^{-1}(kr)^{L+1}, \tag{32}$$

and therefore

$$u^{+}_{\lambda,L,k}(r) = \alpha^{+}_{\lambda,L,k} r^{L+1}\left[1 + \frac{\lambda v_{-1}}{L+1}r + \frac{\lambda^2 v^2_{-1} + (L+1)(\lambda v_0 - \frac{1}{2}k^2)}{(L+1)(2L+3)}r^2 + \cdots\right], \tag{33}$$

with

$$\alpha^{+}_{\lambda,L,k} = \frac{1}{(2L+1)!!}\frac{k^{L+1}}{F_{\lambda,L}(k)}. \tag{34}$$

From all these formulas we get:

$$\begin{aligned} g_{\psi^{+}_{\lambda,\mathbf{k}}}(r) &= \frac{1}{4\pi}\int_{S^2} |\psi^{+}_{\lambda\mathbf{k}}(\mathbf{r})|^2 \,\mathrm{d}\Omega_{\mathbf{r}} = \frac{1}{4\pi} \times \frac{2}{\pi}\sum_L \frac{|u^{+}_{\lambda,L,k}(r)|^2}{k^2 r^2} \sum_{M=-L}^{L} |Y^M_L(\Omega_{\mathbf{k}}|^2 \\ &= \frac{1}{8\pi^3}\sum_L (2L+1)\frac{|\alpha^{+}_{\lambda,L,k}|^2}{k^2} r^{2L} \\ &\quad \times \left[1 + 2\frac{\lambda v_{-1}}{L+1}r + \frac{(4L+5)\lambda^2 v^2_{-1} + 2(L+1)^2(\lambda v_0 - \frac{1}{2}k^2)}{(L+1)^2(2L+3)}r^2 + \cdots\right] \\ &= \frac{1}{8\pi^3}\sum_L \frac{(2L+1)}{[(2L+1)!!]^2}\frac{k^{2L}}{|F_{\lambda,L}(k)|^2} r^{2L} \\ &\quad \times \left[1 + 2\frac{\lambda v_{-1}}{L+1}r + \frac{(4L+5)\lambda^2 v^2_{-1} + 2(L+1)^2(\lambda v_0 - \frac{1}{2}k^2)}{(L+1)^2(2L+3)}r^2 + \cdots\right]. \end{aligned} \tag{35}$$

As in the bound case, only those terms with $L = 0$ contribute to $g_{\psi^+_{\lambda,\mathbf{k}}}(0)$, $g'_{\psi^+_{\lambda,\mathbf{k}}}(0)$, whereas only $L = 0, 1$ terms need to be considered for $g''_{\psi^+_{\lambda,\mathbf{k}}}(0)$:

$$\begin{aligned} g_{\psi^+_{\lambda,\mathbf{k}}}(0) &= \frac{1}{8\pi^3}\frac{1}{|F_{\lambda,0}(k)|^2}, \qquad \mathrm{Cusp}_{\psi^+_{\lambda\mathbf{k}}}(0) = 2\lambda v_{-1}, \\ \mathrm{Curv}_{\psi^+_{\lambda\mathbf{k}}}(0) &= \tfrac{2}{3}\left[5\lambda^2 v_{-1}^2 + 2\left(\lambda v_0 - \frac{1}{2}k^2\right) + \tfrac{k^2|F_{\lambda,0}(k)|^2}{|F_{\lambda,1}(k)|^2}\right]. \end{aligned} \tag{36}$$

The contribution $\rho_{\lambda,\mathrm{sc},E_\mathrm{F}}(r)$ of the scattering states to the density is plainly

$$\rho_{\lambda,\mathrm{sc},E_\mathrm{F}}(r) = 2 \times \int_{|\mathbf{k}|\,\leqslant k_\mathrm{F}} \mathrm{d}^3k\; g_{\psi^+_{\lambda,\mathbf{k}}}(r), \tag{37}$$

where k_F is the Fermi momentum ($E_\mathrm{F} = k_\mathrm{F}^2/2$).

Adding the contributions of all scattering levels:

$$\begin{aligned} \rho_{\lambda,\mathrm{sc},E_\mathrm{F}}(0) &= 2 \times \int_{|\mathbf{k}|\,\leqslant k_\mathrm{F}} \mathrm{d}^3k\; g_{\psi^+_{\lambda,\mathbf{k}}}(0) = \frac{1}{\pi^2}\int_0^{k_\mathrm{F}} \mathrm{d}k\; \frac{k^2}{|F_{\lambda,0}(k)|^2} \\ \rho'_{\lambda,\mathrm{sc},E_\mathrm{F}}(0) &= 2 \times \int_{|\mathbf{k}|\,\leqslant k_\mathrm{F}} \mathrm{d}^3k\; g'_{\psi^+_{\lambda,\mathbf{k}}}(0) = 2\lambda v_{-1}\rho_{\lambda,\mathrm{sc},E_\mathrm{F}}(0) \\ \rho''_{\lambda,\mathrm{sc},E_\mathrm{F}}(0) &= 2 \times \int_{|\mathbf{k}|\,\leqslant k_\mathrm{F}} \mathrm{d}^3k\; g''_{\psi^+_{\lambda,\mathbf{k}}}(0) \\ &= \frac{2}{3}(5\lambda^2 v_{-1}^2 + 2\lambda v_0)\rho_{\lambda,\mathrm{sc},E_\mathrm{F}}(0) + \frac{2}{3\pi^2}\int_0^{k_\mathrm{F}} \mathrm{d}k\; k^4[-|F_{\lambda,0}(k)|^{-2} + |F_{\lambda,1}(k)|^{-2}]. \end{aligned} \tag{38}$$

In the following, we will mathematically prove that $\rho_\lambda(r)$, $\rho'_\lambda(r)$, and $\rho''_\lambda(r)$ are differentiable functions of λ for any $\lambda \geqslant 0$. Each of the individual (bound, scattering) terms in the density present discontinuities at the threshold values of λ for which new bound states appear, but, remarkably enough, they cancel each other. Nevertheless, to prove this cancellation for the general case of an arbitrary finite-range central potential $\lambda V(r)$, we need an auxiliary lemma to express the bound state contribution in terms of the Jost functions. We know [21, 23] that the negative bound energies are associated with the zeros of the Jost functions in the positive imaginary axis. Suppose that $F_{\lambda,L}(\bar{k}) = 0$, where $\bar{k} = \mathrm{i}\bar{\kappa}$, $\bar{\kappa} > 0$, i.e., $\bar{k}$ is a zero of $F_{\lambda,L}(k)$ in the positive imaginary axis, and thus $E = \frac{1}{2}\bar{k}^2 = -\frac{1}{2}\kappa^2$ is a bound energy. We shall write $\alpha_{\lambda,L,\mathrm{i}\bar{\kappa}} = \alpha_{\lambda,L,E}$.

Lemma 1. *Let $u_{\lambda,L,\mathrm{i}\bar{\kappa}}(r)$ be the real regular solution of the L-channel reduced radial differential equation. Suppose that it is of unit norm, i.e.,*

$$\int_0^\infty \mathrm{d}r\; |u_{\lambda,L,\mathrm{i}\bar{\kappa}}(r)|^2 = 1 \tag{39}$$

and that $u_{\lambda,L,\mathrm{i}\bar{\kappa}}(r) \sim \alpha_{\lambda,L,\mathrm{i}\bar{\kappa}} r^{L+1}$ as $r \to 0$. Then

$$|\alpha_{\lambda,L,\mathrm{i}\bar{\kappa}}|^2 = (-1)^{L+1}\frac{4}{((2L+1)!!)^2}\frac{(\bar{\kappa})^{2(L+1)}}{[F_{\lambda,L}(-\mathrm{i}\kappa)\partial_\kappa F_{\lambda,L}(\mathrm{i}\kappa)]_{\kappa=\bar{\kappa}}}. \tag{40}$$

This lemma, whose proof is an extension of well-known result for s-waves [21, 22], is the key to further, pure mathematical analysis the essence of which is summarized below.

We have just paid attention to the cases relevant in our problem: $L = 0$ and $L = 1$. From the behaviour of the Jost functions for $k \to 0$ and $\lambda \to \lambda_{L,n}$,

$$\begin{aligned} F_{\lambda,0}(k) &\sim (-1)^n[\alpha_{0,n}(\lambda - \lambda_{0,n}) + \mathrm{i}\gamma_{0,n}k + \cdots], \\ F_{\lambda,L>0}(k) &\sim (-1)^n[\alpha_{L,n}(\lambda - \lambda_{L,n}) + \beta_{L,n}k^2 + \mathrm{i}\gamma_{L,n}k^3 + \cdots], \end{aligned} \tag{41}$$

where $\alpha_{0,n}, \gamma_{0,n}, \alpha_{L,n}, \beta_{L,n}, \gamma_{L,n}$ are strictly positive, we have proved the following two propositions.

Proposition 1 *The appearance of a new bound state when λ crosses a critical value $\lambda_{L,n}$ accounts for a non-smooth behaviour of $\rho_{\lambda,\mathrm{bd}}(0)$, $\rho''_{\lambda,\mathrm{bd}}(0)$, as functions of λ around $\lambda_{L,n}$. Up to a C^1 function of λ,*

$$\begin{aligned} 4\pi\rho_{\lambda,\mathrm{bd}}(0) &\underset{\lambda\to\lambda_{0,n}}{\sim} 4\alpha_{0,n}\gamma_{0,n}^{-3}(\lambda - \lambda_{0,n})\theta(\lambda - \lambda_{0,n}), \\ 4\pi\rho''_{\lambda,\mathrm{bd}}(0) &\underset{\lambda\to\lambda_{0,n}}{\sim} \tfrac{8}{3}[5\lambda_{0,n}^2 v_{-1}^2 + 2\lambda_{0,n}v_0]\alpha_{0,n}\gamma_{0,n}^{-3}(\lambda - \lambda_{0,n})\theta(\lambda - \lambda_{0,n}), \\ 4\pi\rho''_{\lambda,\mathrm{bd}}(0) &\underset{\lambda\to\lambda_{1,n}}{\sim} [4\alpha_{1,n}\beta_{1,n}^{-4}\gamma_{1,n}(\lambda - \lambda_{1,n}) + 2\alpha_{1,n}^{1/2}\beta_{1,n}^{-5/2}|\lambda - \lambda_{1,n}|^{1/2} + \tfrac{4}{3}\beta_{1,n}^{-1}\gamma_{1,n}^{-1}]\theta(\lambda - \lambda_{1,n}). \end{aligned} \tag{42}$$

Proposition 2 *In a neighbourhood of $\lambda = \lambda_{L,n}$, the quantities $\rho_{\lambda,\mathrm{sc},E_\mathrm{F}}(0)$, $\rho''_{\lambda,\mathrm{sc},E_\mathrm{F}}(0)$ behave as follows, up to a C^1 function of λ:*

$$\begin{aligned} 4\pi\rho_{\lambda,\mathrm{sc},E_\mathrm{F}}(0) &\underset{\lambda\to\lambda_{0,n}}{\sim} -2\alpha_{0,n}\gamma_{0,n}^{-3}|(\lambda - \lambda_{0,n})|, \\ 4\pi\rho''_{\lambda,\mathrm{sc},E_\mathrm{F}}(0) &\underset{\lambda\to\lambda_{0,n}}{\sim} -\tfrac{4}{3}(5\lambda_{0,n}^2 v_{-1}^2 + 2\lambda_{0,n}v_0)\alpha_{0,n}\gamma_{0,n}^{-3}|\lambda - \lambda_{0,n}|, \\ 4\pi\rho''_{\lambda,\mathrm{sc},E_\mathrm{F}}(0) &\underset{\lambda\to\lambda_{1,n}}{\sim} \tfrac{4}{3}\beta_{1,n}^{-1}\gamma_{1,n}^{-1}\theta(-\lambda + \lambda_{1,n}) - 2\alpha_{1,n}^{1/2}\beta_{1,n}^{-5/2}(\lambda - \lambda_{1,n})^{1/2}\theta(\lambda - \lambda_{1,n}) \\ &\quad -4\alpha_{1,n}\beta_{1,n}^{-4}\gamma_{1,n}|\lambda - \lambda_{1,n}|\theta(-\lambda + \lambda_{1,n}). \end{aligned} \tag{43}$$

The above two propositions yield the following theorem, which is in fact the core of the present detailed study.

Theorem.

1. *The density $\rho_{\lambda,E_\mathrm{F}}(0)$ at the origin is a C^1 function of the coupling constant λ.*
2. *The cusp function* $\mathrm{Cusp}(\lambda) = \rho'_\lambda(0)/\rho_\lambda(0)$ *is a linear function:*
$$\mathrm{Cusp}(\lambda) = 2v_{-1}\lambda. \tag{44}$$
3. *The second radial derivative $\rho''_{\lambda,E_\mathrm{F}}(0)$ of the density at the origin is a C^1 function of the coupling constant λ.*

The third point of the theorem, i.e., the differentiability of the *total* curvature $\rho''_{\lambda,E_\mathrm{F}}(0)$ as a function of λ is the most relevant for our purposes: it refers to the main goal of our study.

It means that no discontinuities in $\rho''_{\lambda,E_\mathrm{F}}(0)$ are expected whenever λ reaches the threshold for the appearance of a new bound state in extended electron systems.

3. Illustrative results

3.1. Hulthén potential

The continuity of $\rho''_{\lambda,E_F}(0)$ across the λ thresholds can be illustrated through particular examples. Let us consider the Hulthén potential $\lambda V(r)$

$$V(r) = -\frac{1/a}{e^{r/a}-1}, \tag{45}$$

in which $\lambda, a > 0$. Now

$$v_j = -B_{j+1}(0)a^{-(j+1)}/(j+1)!, \quad j \geqslant -1, \tag{46}$$

in terms of the Bernoulli numbers.

The Hamiltonian $H = -\frac{1}{2}\Delta + \lambda V$ has a finite (possibly zero) number of bound states. For those with $L = 0$ explicit expressions are available [18]:

$$\psi_{\lambda,0,0,E_{n0}}(\mathbf{r}) = R_{\lambda,0,E_{n0}}(r)Y_0^0(\Omega_{\mathbf{r}}), \tag{47}$$

where

$$R_{\lambda,0,E_{n0}}(r) = 2\lambda^{1/2}(\lambda^2 - n^4/a^2)^{1/2}n^{-3/2}(r/a)^{-1}(e^{r/a}-1) \times e^{(-2+n-2\lambda a/n)r/2a} \times {}_2F_1(1-n, 1+2\lambda a/n, 2, 1-e^{-r/a}) \tag{48}$$

and

$$E_{n0} = -\tfrac{1}{2}(\lambda/n - n/2a)^2, \quad n = 1, 2, \ldots, \lceil\sqrt{2\lambda a}\rceil - 1. \tag{49}$$

Therefore when $2(\lambda a) = \{1^2, 2^2, \ldots\}$ there are $L = 0$ resonances at zero energy. Each of these critical or threshold values $2(\lambda a)_{0,n} = n^2$ mark the appearance of a new $L = 0$ eigenstate for any $\lambda a > (\lambda a)_{0,n}$.

The explicit calculation with the above radial functions yields

$$\begin{aligned} g'_{\psi_{\lambda,0,0,E_n}}(0)/g_{\psi_{\lambda,0,0,E_n}}(0) &= -2\lambda, \\ g''_{\psi_{\lambda,0,0,E_n}}(0)/g_{\psi_{\lambda,0,0,E_n}}(0) &= \tfrac{1}{6}(20\lambda^2 + 4\lambda^2/n^2 + n^2/a^2) = \tfrac{2}{3}[5\lambda^2 + 2(\lambda/2a - E_{n0})]. \end{aligned} \tag{50}$$

With $\lambda = Z$ for the strength and $a = (2Z)^{-1}$ for the *critical* ($E_{n0} = 0$) screening at $n = 1$ the right-hand side of equation (50) becomes $(14/3)Z^2$, showing the role of screening. The s-type Coulombic value is $(10/3)Z^2$ at vanishing ($n \to \infty$) binding, as will be seen in equation (77) below.

Furthermore, and because in the critically screened case $k^2|F_{\lambda,0}(k)|^2/|F_{\lambda,1}(k)|^2 = 0$ at $k = 0$, one also gets the same $(14/3)Z^2$ value now from equation (36) for $\mathrm{Curv}_{\psi^+_{\lambda,\mathbf{k}}}(0)$. There is a deviation from the Coulombic scattering-value, $(12/3)Z^2$, obtained with *s and p* states in equation (85) below.

For eigenfunctions with $L \geqslant 1$ no explicit analytic expression is known, and one has to resort to numerical computation. For instance,

$$\begin{aligned}(\lambda a)_{1,n} &= \{2.6530, 5.3626, 9.0504, \ldots\}\\ (\lambda a)_{2,n} &= \{6.343, 10.26, 15.10, \ldots\}\\ (\lambda a)_{3,n} &= \{11.6, 16.7, 22.9, \ldots\}\\ &\ldots.\end{aligned} \tag{51}$$

Consider now the scattering states under the Hulthén potential. To simplify the notation, we take $a = 1$ without loss of generality. The Jost function $F_{\lambda,0}$ is explicitly known:

$$F_{\lambda,0}(k) = {}_2F_1(-\mathrm{i}k + \mathrm{i}(k^2 - 2\lambda)^{1/2}, -\mathrm{i}k - \mathrm{i}(k^2 - 2\lambda)^{1/2}, 1 - 2\mathrm{i}k; 1). \tag{52}$$

Not so $F_{\lambda,1}$, which we calculate numerically. One notes that there is a nontrivial dependence on k, but that asymptotically

$$\tfrac{2}{3}k^2[|F_0(k)/F_1(k)|^2 - 1] \underset{k\to\infty}{\sim} \tfrac{2}{3}\lambda(\lambda - 1) \tag{53}$$

so that the Coulomb behaviour is restored at high energies:

$$g''_{\psi^+_{\lambda,\mathbf{k}}}(0)/g_{\psi^+_{\lambda,\mathbf{k}}}(0) \underset{k\to\infty}{\sim} 4\lambda^2, \tag{54}$$

as physically expected.

We proceed now to analyse the local behaviour of the total $\rho_{\lambda,E_\mathrm{F}}(r) = \rho_{\lambda,\mathrm{bd}} + \rho_{\lambda,\mathrm{sc},E_\mathrm{F}}$ around the thresholds. The first threshold value of the coupling constant is $\lambda = 1/2$. By straightforward expansions for the radial solutions and Jost functions at the origin, one can show ($a = 1$) that

$$\begin{aligned}g_{\psi_{\lambda,0,0,E_{1,0}}} &= \frac{1}{8\pi}z[(2+3z)^2 - (2+3z)(2+7z)r + (7/3 + 15z + 85z^2/4)r^2 + \mathcal{O}(r^3)],\\ g_{\psi^+_{\lambda,0,0,k}}(r) &= \frac{1}{8\pi^3|F_{\lambda,0}(k)|^2}[1 - (1+2z)r + (7/12 - k^2/3 + 2z - 5z^2/3)r^2 + \mathcal{O}(r^3)],\\ g_{\psi^+_{\lambda,1,0,k}}(r) &= \frac{1}{24\pi^3|F_{\lambda,1}(k)|^2}k^2r^2[1 + \mathcal{O}(r)].\end{aligned} \tag{55}$$

Here $z = \lambda - (1/2)$; similar expressions hold around *each* of the other critical values $\lambda_{0,n}$.

Now, we illustrate the behaviours of the bound and scattering densities. Figure 1 shows $\rho_{\lambda,\mathrm{bd}}(0)$ as a function of λ, where

$$\rho_{\lambda,\mathrm{bd}}(r) = 2 \times \sum_{nLM} g_{\psi_{\lambda,LM,E_{n,L}}}(r), \tag{56}$$

and the *discontinuity* in its slope when λ crosses the first and second thresholds $\lambda = 0.5, 2$. In addition, one may see that $\rho_{\lambda,\mathrm{bd}}(0) \propto \lambda^3$ for $\lambda \gg 1$.

Since the Jost function $F_{\lambda,L}$ vanishes [21, 23] when a new L-wave resonance or eigenstate appears at zero energy, the associated density from individual long wave modes diverges as

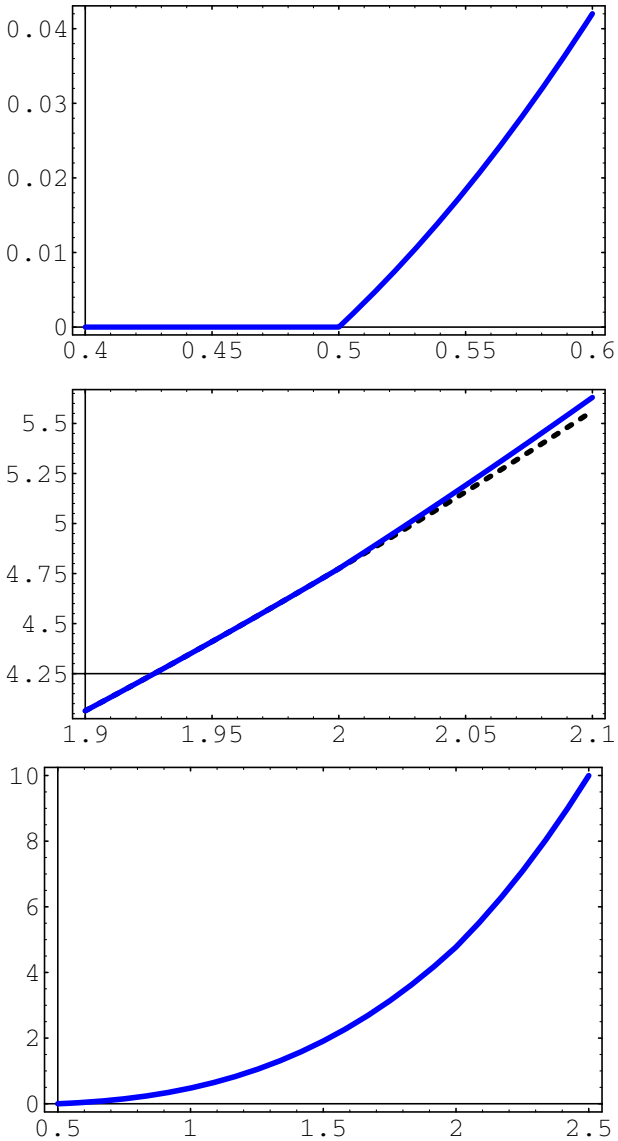

Figure 1. Graphs of the density at the origin due to bound states $\rho_{\lambda,\mathrm{bd}}(0)$ for the Hulthén potential, as a function of the coupling constant λ. The dotted line represents the contribution of the first bound state, which is the sole contributor for $\lambda \leqslant 2$. A zoom around the threshold values of λ is shown in the two upper panels.

equation (55) clearly heralds. However this divergence is smoothed upon integrating over momenta up to the Fermi level $k_{\mathrm{F}} > 0$. This is in complete agreement with an earlier result [16] obtained for $L = 0$, and shows that the Fermi–Dirac distribution function of electrons has a very important role in the screening action of an extended system.

For the scattering density

$$\rho_{\lambda,\mathrm{sc},E_{\mathrm{F}}}(r) = 2 \times \int_{|\mathbf{k}| \leqslant k_{\mathrm{F}}} \mathrm{d}^3k \; g_{\psi^+_{\lambda,\mathbf{k}}}(r), \tag{57}$$

one obtains the top panel in figure 2 for $k_F = 0.5, 1, 1.5, 2$. The spiky maxima are located at the s-waves threshold values $\lambda = n^2/2$ and increase linearly with λ. When the discrete and continuum contributions are added the discontinuity in the slope at the critical coupling constants disappears.

This is illustrated by the remaining graphs in figure 2. The precise argument, as an extension of the result [16] obtained for $n = 1$ and $L = 0$, to arbitrary n and $L = 1$ reads as follows. We have the important quantities

$$\rho_{\lambda,E_F}(0) = g_{\lambda,\mathrm{bd}}(0) + g_{\lambda,\mathrm{sc},E_F}(0), \qquad \rho''_{\lambda,E_F}(0) = g''_{\lambda,\mathrm{bd}}(0) + g''_{\lambda,\mathrm{sc},E_F}(0), \tag{58}$$

where, in our case

$$g_{\lambda,\mathrm{bd}}(0) = \sum_{n=1}^{\lfloor\sqrt{2\lambda}\rfloor} (-n^4\lambda + 4\lambda^3)/2\pi n^3, \qquad g_{\lambda,\mathrm{sc},E_F}(0) = \frac{1}{\pi^2}\int_0^{k_F} \mathrm{d}k \frac{k^2}{|F_{\lambda,0}(k)|^2}, \tag{59}$$

and

$$\begin{aligned} g''_{\lambda,\mathrm{bd}}(0) &= -\sum_{n=1}^{\lfloor\sqrt{2\lambda}\rfloor} (n^8\lambda + 20n^6\lambda^3 - 16\lambda^5 - 80n^2\lambda^5)/12\pi n^5, \\ g''_{\lambda,\mathrm{sc},E_F}(0) &= \frac{2}{3\pi^2}[\lambda(5\lambda+1)A - B + C], \end{aligned} \tag{60}$$

with

$$A = \int_0^{k_F} \mathrm{d}k \frac{k^2}{|F_{\lambda,0}(k)|^2}, \qquad B = \int_0^{k_F} \mathrm{d}k \frac{k^4}{|F_{\lambda,0}(k)|^2}, \qquad C = \int_0^{k_F} \mathrm{d}k \frac{k^4}{|F_{\lambda,1}(k)|^2}. \tag{61}$$

It is obvious that the slope discontinuity at $\lambda_{0,n} = n^2/2$ in the scattering term is entirely due to the integral over momenta arbitrarily close to $k = 0$, and thus it is independent of the value of $k_F > 0$. It suffices thus to compute it for k_F infinitesimally small but positive. But in this case we may use the following asymptotic expression for λ close to the s-wave threshold $\lambda_{0,n} = \frac{1}{2}n^2$:

$$|F_{\lambda,0}(k)|^2 \sim n^{-4}(\lambda - \tfrac{1}{2}n^2)^2 + n^{-2}k^2 + O((\lambda - \tfrac{1}{2}n^2)^3, k^3, (\lambda - \tfrac{1}{2}n^2)k^2). \tag{62}$$

Hence

$$\int_0^{k_F} \mathrm{d}k \frac{k^2}{|F_{\lambda,0}(k)|^2} \sim n^2 k_F - n|\lambda - \tfrac{1}{2}n^2| \tan^{-1}(nk_F/|\lambda - \tfrac{1}{2}n^2|), \tag{63}$$

and therefore the change $\triangle\delta_{\mathrm{sc},n}$ in the slope of $\rho_{\lambda,\mathrm{sc},E_F}(0)$ when λ crosses the nth s-wave threshold is exactly

$$\triangle\delta_{\mathrm{sc},n} = (2 \times 4\pi)(1/8\pi^3)(-n\pi) = -n/\pi, \tag{64}$$

whereas the change $\triangle\delta_{\mathrm{bd},n}$ due to the onset of the bound state is

$$\triangle\delta_{\mathrm{bd},n} = 2 \times [\partial_\lambda(-n\lambda + 4n^{-3}\lambda^3)/4\pi]_{\lambda=\lambda_{0,n}} = n/\pi. \tag{65}$$

The sum of these equations is zero; one has a smooth character.

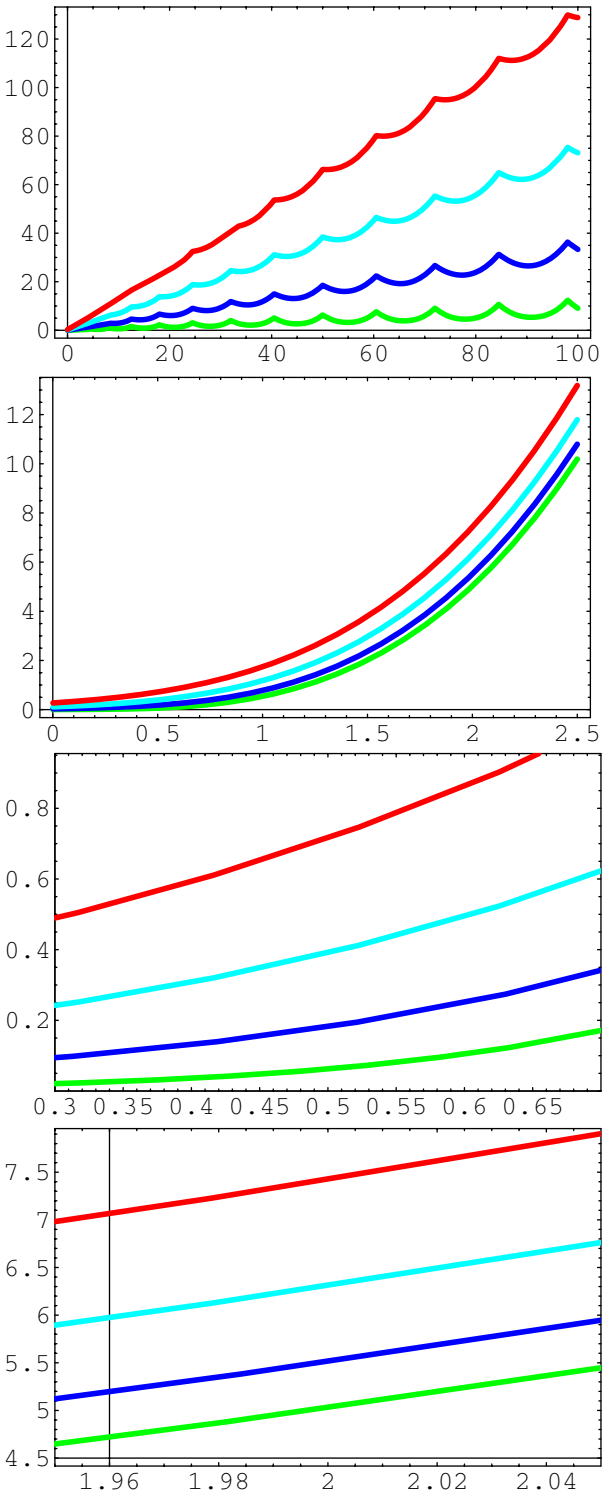

Figure 2. Graphs of the density at the origin for the Hulthén potential due to scattering states ($\rho_{\lambda,\mathrm{sc},E_\mathrm{F}}(0)$, above) and all states ($\rho_{\lambda,E_\mathrm{F}}(0)$, rest), as a function of the coupling constant λ. The vicinity of the first λ threshold values is shown in more detail in the two lower panels. Lines from bottom up show different values of $k_\mathrm{F} = 0.5, 1, 1.5, 2$.

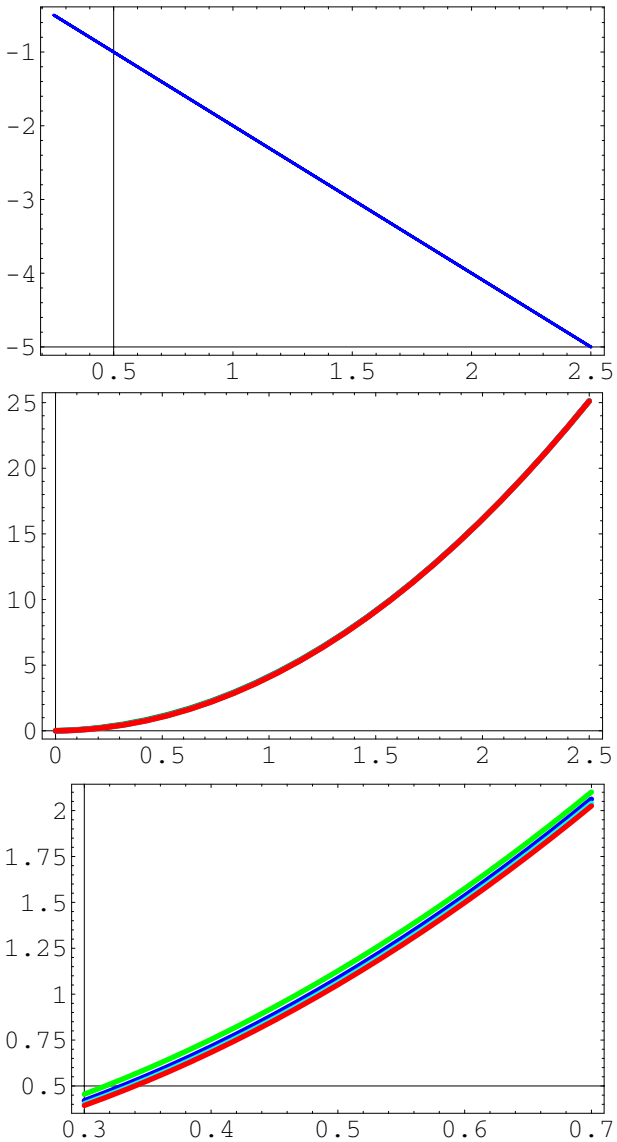

Figure 3. Graphs of the cusp ($\rho'_{\lambda,E_F}(0)$, upper panel) and the curvature ($\rho''_{\lambda,E_F}(0)$, middle panel) at the origin due to all states, for a Hulthén potential and as a function of the coupling constant λ. The curves correspond to $k_F = 0.5, 1, 1.5, 2$ from bottom up. All curves merge into a single one for $\rho'_{\lambda,E_F}(0)$. The lower panel shows in more detail the vicinity of the first threshold value $\lambda = 1/2$.

The cusp $\mathrm{Cusp}_{\lambda,E_F}(0) = \rho'_{\lambda,E_F}(0)/\rho_{\lambda,E_F}(0)$ at the origin $r = 0$ is shown in figure 3 for $k_F = 0.5, 1, 1.5, 2$. All the curves are exactly the same, as expected, since the cusp behaves exactly as -2λ for all λ, k_F, as we know. Finally, let us look at the curvature $\mathrm{Curv}_{\lambda,E_F}(0) = \rho''_{\lambda,E_F}(0)/\rho_{\lambda,E_F}(0)$ at the origin $r = 0$ for a Hulthén potential of strength λ. We show it in figure 3 for $k_F = 0.5, 1, 1.5, 2$. It behaves as λ^2 for large λ. Amazingly enough, no signal of discontinuity shows up ostensibly in the curvature.

Let us prove this analytically. Since we have seen that the slope of $\rho_{\lambda,E_F}(0)$ depends continuously on λ, it is enough to look at the behaviour of $\rho''_{\lambda,E_F}(0)$ as a function of λ.

The slope of $g''_{\lambda,\mathrm{bd}}(0)$ presents a discontinuity at $\lambda_{0,n}$ given by

$$\triangle\bar{\delta}_{\mathrm{bd},n} = \frac{1}{6\pi}n^3(2+5n^2). \tag{66}$$

Regarding $g''_{\lambda,\mathrm{sc},E_\mathrm{F}}(0)$, the terms B, C have continuous slopes, while the slope of A changes by $-n/4$ when crossing $\lambda_{0,n}$. Therefore

$$\triangle\bar{\delta}_{\mathrm{sc},n} = \frac{2}{3\pi^2}\lambda_{0,n}(5\lambda_{0,n}+1)(-n\pi) = -\frac{1}{6\pi}n^3(2+5n^2) \tag{67}$$

and the sum of these equations is zero; one has a smooth character.

The smoothness of the density, the cusp and the curvature at the origin in the vicinity of the thresholds for the appearance of the first ($L=0$)- and ($L=1$)-bound states ($\lambda=\lambda_{0,1}$ and $\lambda=\lambda_{1,1}$ respectively) is summarized in figures 4 and 5. The compensation between the bound and scattering sectors at the thresholds is distinctly shown in them.

3.2. Friedel's sum rule for local potentials

For real electron gases with Fermi momentum k_F the strength λ of a Coulomb impurity is not arbitrary, but it has to satisfy an approximate consistency relation known as Friedel's sum rule, necessary for total screening at large distances:

$$\lambda = F_\lambda(k_\mathrm{F}) = \frac{2}{\pi}\sum_{L\geqslant 0}(2L+1)\delta_{\lambda,L}(k_\mathrm{F}), \tag{68}$$

where $\delta_{\lambda,L}$ are the phase shifts produced by $\lambda V(r)$ and $V(r)$ (with $v_{-1}=-1$) is fixed.

In the numerical computation of the r.h.s. of equation (68) the phase shifts are to be chosen continuously form the value 0 at high momenta. We will illustrate this with several examples.

Before presenting some examples, let us discuss the convergence of the Friedel sum and its high-energy limit. For a given k, the infinite series $F_\lambda(k)$ converges rapidly since the phase shift has generically the following behaviour for large L [21, 23, 24]:

$$\delta_{\lambda,L}(k) = o(\mathrm{e}^{-\alpha(k)L}) \quad \text{for } L\gg 1, \quad \cosh\alpha(k) = 1+(2k^2)^{-1}, \tag{69}$$

for potentials of unit range. However, a rather accurate calculation of $F_\lambda(k)$ may require taking into account some tens of angular momenta. For instance, for the Hulthén potential of equation (45) with $a=1$, and with reasonable values, say $\lambda=3$, $k=1.5$, the truncated series

$$F_{\lambda,L_0}(k) = \frac{2}{\pi}\sum_{0\leqslant L\leqslant L_0}(2L+1)\delta_{\lambda,L}(k) \tag{70}$$

yields the following values:

$$\begin{aligned} &F_{3,0}(1.5) = 2.14371,\ F_{3,1}(1.5) = 6.03127,\ F_{3,5}(1.5) = 14.5148,\\ &F_{3,10}(1.5) = 16.0700,\ F_{3,25}(1.5) = 16.1968,\ F_{3,50}(1.5) = 16.1968. \end{aligned} \tag{71}$$

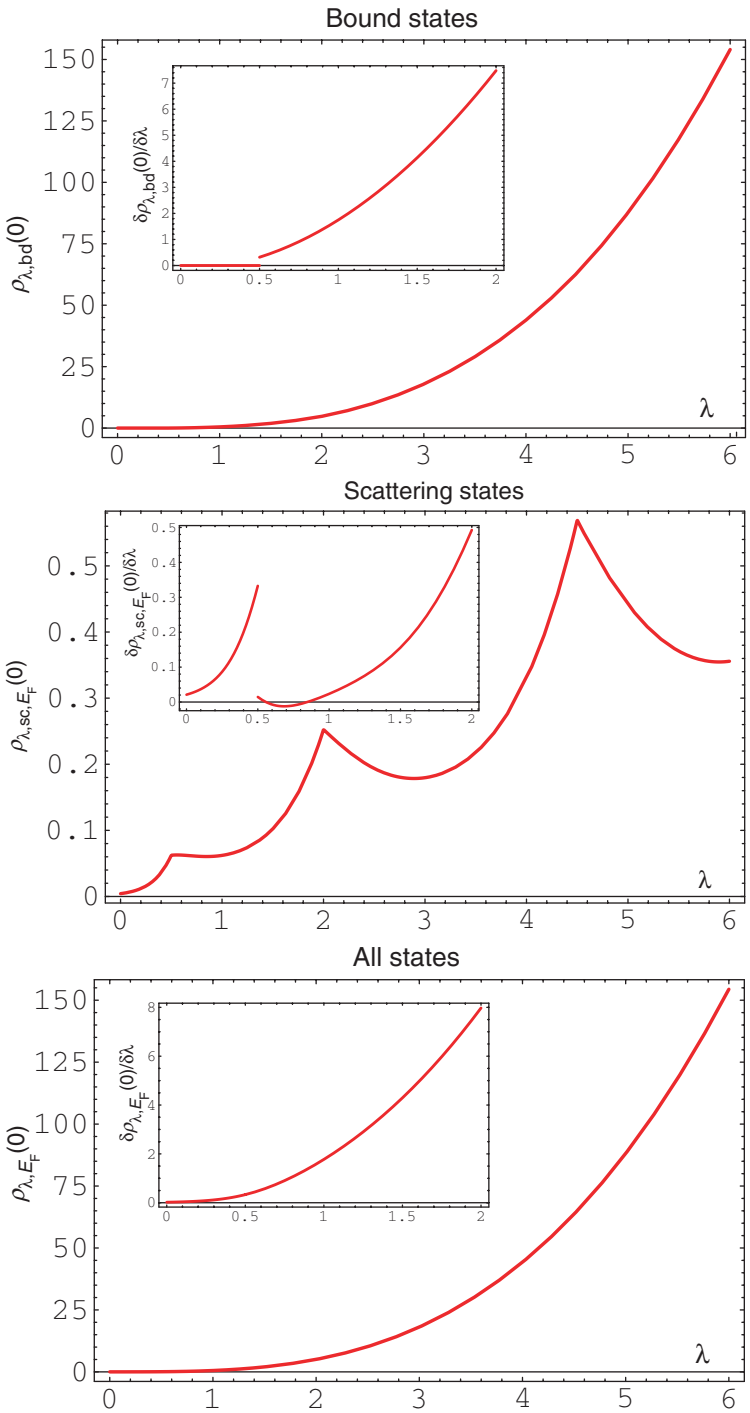

Figure 4. Partial components of the electronic density at the origin $\rho_{\lambda,\mathrm{bd}}(0)$ (upper panel) and $\rho_{\lambda,\mathrm{sc},E_\mathrm{F}}(0)$ (middle panel) as a function of the coupling constant λ for a Hulthén potential $\lambda V(r) = -\lambda/(\mathrm{e}^r - 1)$. The total density $\rho_{\lambda,E_\mathrm{F}}(0) = \rho_{\lambda,\mathrm{bd}}(0) + \rho_{\lambda,\mathrm{sc},E_\mathrm{F}}(0)$ is shown as well in the lower panel. The insets show the derivatives of these functions with respect to λ ($\delta\rho_{\lambda,\mathrm{bd}}(0)/\delta\lambda$, $\delta\rho_{\lambda,\mathrm{sc},E_\mathrm{F}}(0)/\delta\lambda$, and $\delta\rho_{\lambda,E_\mathrm{F}}(0)/\delta\lambda$ in the upper, middle, and lower panels respectively) in the vicinity of the threshold $\lambda = \lambda_{0,1}$ for the appearance of the first ($L = 0$)-bound state.

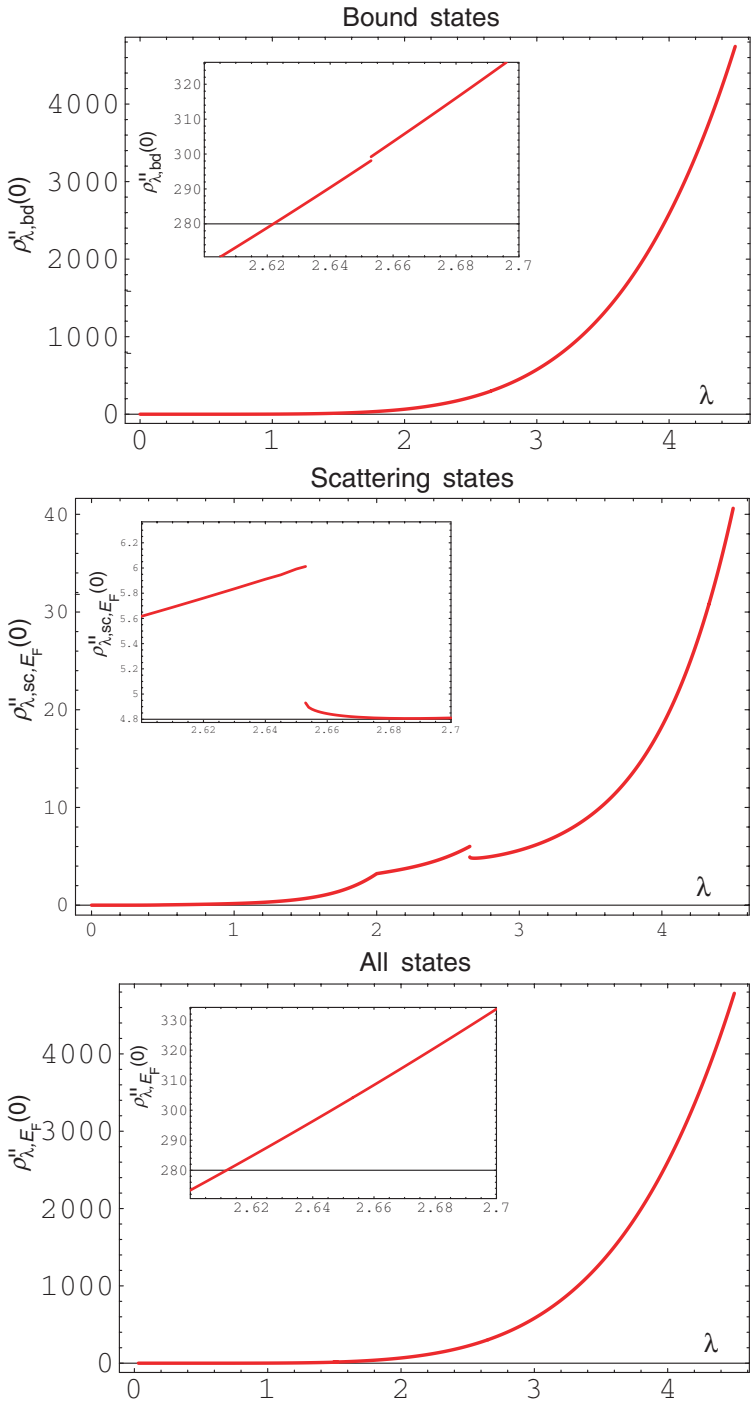

Figure 5. Partial components of the curvature at the origin $\rho''_{\lambda,\mathrm{bd}}(0)$ (upper panel) and $\rho''_{\lambda,\mathrm{sc},E_\mathrm{F}}(0)$ (middle panel) as a function of the coupling constant λ for a Hulthén potential $\lambda V(r) = -\lambda/(\mathrm{e}^r - 1)$. The total curvature $\rho''_\lambda(0) = \rho''_{\lambda,\mathrm{bd}}(0) + \rho''_{\lambda,\mathrm{sc},E_\mathrm{F}}(0)$ is shown as well in the lower panel. The insets show the same functions in the vicinity of the threshold $\lambda = \lambda_{1,1}$ for the appearance of the first $(L = 1)$-bound state.

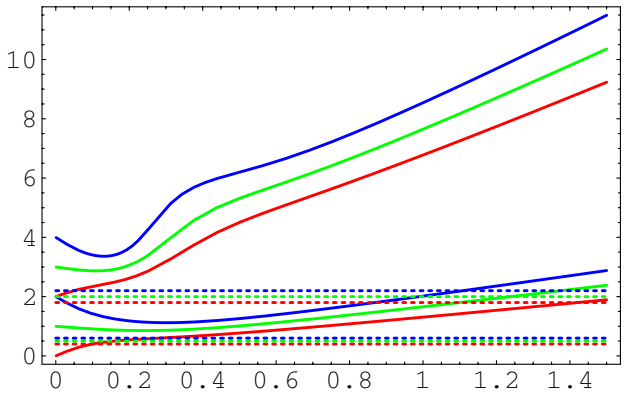

Figure 6. Graph of $F_\lambda(k)$ as a function of k, for a Hulthén potential with the following values for λ: 0.4, $\lambda_{0,1} = 0.5$, 0.6, 1.8, $\lambda_{0,2} = 2.0$, 2.2 (from bottom up).

On the other hand, at high energies the phase shifts are small and therefore it is appropriate using the Born approximation, so that

$$F_\lambda(k) \underset{k\to\infty}{\sim} \frac{2}{\pi}\sum_{0\leqslant L}(2L+1)\,\mathrm{e}^{\mathrm{i}\delta_{\lambda,L}(k)}\sin\delta_{\lambda,L}(k) \underset{k\to\infty}{\sim} \frac{4}{\pi}\lambda\, k\int_0^\infty \mathrm{d}r\, r^2 V(r). \tag{72}$$

Thus the Friedel sum increases linearly with k for large momenta.

In figure 6, we have plotted $F_\lambda(k)$ for several values of the strength parameter λ, in the particular case of a Hulthén potential with $a = 1$. The linear behaviour of $F_\lambda(k)$ for large k is conspicuous. To compute numerically this function with sufficient accuracy we have added up those terms in Friedel sum up to a limiting angular momentum $L_0 = 25$. Levinson's theorem [23] can be read off from these graphs. In fact, observe that

$$F_\lambda(0) = \frac{2}{\pi}\sum_{\lambda_{L,n}\leqslant\lambda}(2L+1)\pi - \frac{2}{\pi}\sum_{\lambda_{0,n}=\lambda}\frac{\pi}{2} = 2N_{\mathrm{bs},E\leqslant 0}(H_\lambda) + N_{\mathrm{zer},L=0}(H_\lambda), \tag{73}$$

where $N_{\mathrm{bs},E\leqslant 0}(H_\lambda)$, $N_{\mathrm{zer},L=0}(H_\lambda)$ stand for the number of bound states and zero-energy resonances, respectively.

The intersection of the dotted lines, representing the values of λ, with the corresponding graph of $F_\lambda(k)$ mark the solutions to equation (68). Note that, in the particular case of the Hulthén potential with fixed $a = 1$, i.e., with a range equal to the atomic Bohr radius a_B, this equation may have no solution. However, if we allow for an arbitrary range a in equation (45), then Friedel's sum rule becomes

$$\lambda = \frac{2}{\pi}\sum_{L\geqslant 0}(2L+1)\delta_{\lambda a/a_\mathrm{B},L}(k_\mathrm{F}a/a_\mathrm{B}). \tag{74}$$

Therefore, for any given Coulomb strength λ and Fermi momentum k_F, there exists some range a for which the sum rule is fulfilled.

4. Coulomb potential

The Coulomb potential $\lambda V(r)$, with $V(r) = -1/r$, and $\lambda > 0$ is not representative of the screening problem in which this study is focused and requires a separate treatment. It is included in this section because of its general importance. For the Coulomb case, $v_{-1} = -1$, $v_j = 0$, $j \geqslant 0$. Suppose first a bound state with energy $E_n = -\lambda^2/2n^2$, with definite angular momentum quantum numbers. Its normalized eigenfunction may be taken of the form

$$\psi_{\lambda,LM,E_n}(\mathbf{r}) = R_{\lambda,L,E_n}(r)Y_L^M(\Omega_\mathbf{r}) \tag{75}$$

where

$$R_{\lambda,L,E_n}(r) = (2\lambda^{3/2}/n^2)[(n-L-1)!/(n+L)!]^{1/2}\bar{r}^L \exp[-\bar{r}/2]L_{n-L-1}^{2L+1}(\bar{r}), \tag{76}$$

with $\bar{r} = 2\lambda r/n$. An explicit calculation shows that

$$\begin{aligned} &g_{\psi_{\lambda,LM,E_n}}(0) = \tfrac{1}{\pi}(\lambda/n)^3\delta_{L,0}, \qquad g'_{\psi_{\lambda,LM,E_n}}(0) = -2\lambda g_{\psi_{\lambda,LM,E_n}}(0)\delta_{L,0}, \\ &g''_{\psi_{\lambda,0,0,E_n}}(0) = \tfrac{2}{3\pi}(5\lambda^2 - 2E_n)(\lambda/n)^3, \qquad g''_{\psi_{\lambda,1,M,E_n}}(0) = \tfrac{2}{9\pi}(\lambda^2 + 2E_n)(\lambda/n)^3, \end{aligned} \tag{77}$$

where the second and third are compatible indeed with equation (21), as expected.

An appropriate (coherent or incoherent) superposition of Coulomb bound states eliminates in the second derivative the energy dependence. Suppose that

$$\psi_{\lambda,n}(\mathbf{r}) = \alpha\psi_{\lambda,0,0,E_n}(\mathbf{r}) + \beta_{-1}\psi_{\lambda,1,-1,E_n}(\mathbf{r}) + \beta_0\psi_{\lambda,1,0,E_n}(\mathbf{r}) + \beta_{+1}\psi_{\lambda,1,+1,E_n}(\mathbf{r}) + (L \geqslant 2) \text{ waves}. \tag{78}$$

Due to the orthogonality of the spherical harmonics the angular integration erases the interferences between the different partial waves entering $\psi_{\lambda,n}$ and thus

$$\begin{aligned} &g_{\psi_{\lambda,n}}(0) = |\alpha|^2 g_{\psi_{\lambda,0,0,E_n}}(0), \qquad g'_{\psi_{\lambda,n}}(0) = -2\lambda\, g_{\psi_{\lambda,n}}, \\ &g''_{\psi_{\lambda,n}}(0) = |\alpha|^2 g''_{\psi_{\lambda,0,0,E_n}}(0) + \sum_M |\beta_M|^2 g''_{\psi_{\lambda,1,M,E_n}}(0). \end{aligned} \tag{79}$$

Consequently, the curvature at the origin for $\psi_{\lambda,n}$ is

$$\mathrm{Curv}_{\psi_{\lambda,n}}(0) = \frac{2}{3}\left[5\lambda^2 + (\lambda/n)^2 + \frac{\sum_M |\beta_M|^2}{3|\alpha|^2}[\lambda^2 - (\lambda/n)^2]\right]. \tag{80}$$

The value of the curvature for bound states is thus independent of n if and only if

$$\sum_M |\beta_M|^2 = 3|\alpha|^2, \tag{81}$$

i.e. if the s and p waves are equally weighted in $\psi_{\lambda,n}$. In that particular case, equation (80) becomes

$$\mathrm{Curv}_{\psi_{\lambda,n}}(0) = 4\lambda^2. \tag{82}$$

Now we consider the scattering states by using the *general* formula involving the Jost functions. We know that, for the Coulomb potential $\lambda V(r)$, with $V(r) = -1/r$ [21]–[23],

$$F_{\lambda,L}(k) = \mathrm{e}^{-\pi\lambda/2k}\Gamma(L+1)/\,\Gamma(L+1-\mathrm{i}\lambda/k) \tag{83}$$

and therefore

$$|F_{\lambda,0}(k)/F_{\lambda,1}(k)|^2 = 1 + (\lambda/k)^2. \tag{84}$$

Thus application of equations (21), (34) and (84) yields

$$\mathrm{Curv}_{\psi^+_{\lambda,\mathbf{k}}}(0) = 2\left[\tfrac{1}{3}(5\lambda^2 + 2(0 - \tfrac{1}{2}k^2)) + \tfrac{1}{3}k^2(1 + (\lambda/k)^2)\right] = 4\lambda^2. \tag{85}$$

We stress that $k^2|F_{\lambda,0}(k)/F_{\lambda,1}(k)|^2$ is now *finite* at $k = 0$ in contrast with the Hulthén-case at critical screening where the same limit for the corresponding product is *zero*. Furthermore, we wish to emphasize that exactly the same values for the investigated quantities are obtained by using Coulomb scattering wavefunctions with definite energy $\frac{1}{2}k^2$ and angular momenta L, M.

Finally, equation (80) shows, as we already mentioned at equation (50) in discussing the critically screened limit for the Hulthén-case, that the restriction to the $L = 0$ sector leads to the same value of the curvature at the origin when the zero energy is approached either from below (bound states) or from above (scattering states), namely,

$$\mathrm{Curv}_{\psi_{E=0,L=0}}(0) = \frac{10}{3}\lambda^2. \tag{86}$$

Discontinuity in the curvature value between the bound and scattering sectors would only appear *if* a different partial-wave symmetry (i.e., a different weight in the $L = 0$ and $L = 1$ contributions to the total sum) was chosen for each of the sectors [25]. It is worth to mention that, if such a choice was made, the discontinuity would also appear in the density $\rho_\lambda(r)$ and its first derivative $\rho'_\lambda(r)$ for any value $r \neq 0$. In the case of a bare Coulomb potential, for which the bound states with equal n-quantum number are energy degenerate, it is hard to imagine a physical situation in which different L-symmetries for the bound and scattering states could appear. And for the potentials of interest in the screening problem, we have seen in the previous section that continuity in $\rho''_\lambda(0)$ is guaranteed in any case.

5. Summary and conclusions

Structural properties of the spherically averaged total charge density $\rho_\lambda(r)$ of a degenerate free electron gas distorted by the action of an attractive, screened potential $\lambda V(r)$ have been investigated in this study. The expected importance of the Fermi–Dirac distribution function to obtain smooth, analytical behaviours for physical averages is verified. The key role of Jost-functions, as scattering characteristics on the complex-plane, to a rigorous analysis on smoothness is pointed out as well.

It is shown in a transparent and unified manner that the $\rho_\lambda(0)$, $\rho'_\lambda(0)$, and $\rho''_\lambda(0)$ quantities are differentiable functions of λ for any $\lambda \geqslant 0$. Hence there are no discontinuities in λ that could be used as imprints for the appearance of bound states. The Hulthén potential is used as an example

to show the smoothness of the curvature $\rho''_\lambda(0)$ at the threshold values of λ for which new bound states appear.

The results obtained unify and extend previous scattered knowledge in an important field of applied relevance. In particular, the smooth behaviour of $\rho''_\lambda(r)$ at small r shows that the curvature does not provide a criterion for the bound-to-free transition in ground-state screening in extended metallic environments, at the usual mean-field level, contrary to the claims of [25].

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