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On Thomas–Fermi–von Weizsäcker and Hartree energies as functions of the degree of ionisation

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Abstract. The properties of Thomas–Fermi–von Weizsäcker energies as functions of the degree of ionisation are studied. A concavity result is established, which can be interpreted as a bound to the decrease of the ionisation energies. A numerical calculation of Hartree energies is described and the critical ionisation is numerically calculated as 1.21.

1. Introduction and summary

In Thomas–Fermi–von Weizsäcker (TFW) theory, the energy of an electron density σ in an external potential $U(x)$ is given by the TFW functional

$$\mathscr{E}_{\mathrm{TFW}}(\sigma) = A\int (\nabla\sigma^{1/2})^2\,\mathrm{d}^3x + Bp^{-1}\int \sigma^p(x)\,\mathrm{d}^3x + \int U(x)\sigma(x)\,\mathrm{d}^3x + \tfrac{1}{2}\|\sigma\|_C^2. \qquad (1)$$

The last term

$$\|\sigma\|_C^2 = \int \sigma(x)\sigma(y)|x-y|^{-1}\,\mathrm{d}^3x\,\mathrm{d}^3y, \qquad (2)$$

accounts for the mutual repulsion of electrons. $U(x)$ is the potential generated by the nucleus, or by a collection of nuclei. The first term is the kinetic energy as in quantum theory for a single electron density, the second term is the kinetic energy as in Thomas–Fermi (TF) theory for a many electron density. There, p is usually chosen as $\frac{5}{3}$. A and B are positive constants. The boundary cases $B=0$ or $A=0$ correspond to the simple Hartree equation (as is used for the Helium atom), or to TF theory, respectively. They can be derived as $Z\to\infty$ limits of the quantum theory for bosonic or fermionic atoms (Benguria and Lieb 1983, Lieb and Simon 1977, Baumgartner 1976). In this context, it has turned out that the Hartree equation is important for the question of the existence of very negative ions. The mathematics of this paper covers the case $B=0$, but we have to demand strict positivity of A.

For an atom with nuclear charge Z and N electrons one has $U(x)=-Z/|x|$ and $\|\sigma\|_1 = \int|\sigma(x)|\,\mathrm{d}^3x = N$, but by extracting a factor Z^2 from all energies, ($\mathscr{E}_{\mathrm{TFW}} \to Z^{-2}\mathscr{E}_{\mathrm{TFW}}$) this case is described by the functional with $U(x)=-1/|x|$ and with $\|\sigma\|_1 = N/Z$. We denote this ratio, which measures the degree of ionisation, by t and study the function

$$E(t) = \inf_{\substack{\sigma\geq 0,\|\sigma\|_1=t\\ \|\sigma\|_C<\infty,\|\sigma\|_p<\infty}} \mathscr{E}_{\mathrm{TFW}}(\sigma), \qquad (3)$$

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$E(t)$ is the renormalised total energy (renormalised by the factor Z^3 in case of the Hartree theory, by $Z^{7/3}$ in case of the TF theory).

We also study

$$e(t)=t^{-1}E(t), \tag{4}$$

which is the renormalised energy per electron (renormalised by Z^2 in Hartree theory, by $Z^{4/3}$ in TF theory).

The question of the existence of TFW theory and some properties of $E(t)$ have been extensively studied (Benguria 1981, Benguria *et al* 1981, Lieb 1981). In this paper we derive some properties of $e(t)$ and other energy terms which seem to be new. The new results appear in theorem 2, (i) and (vi) through (x), and in theorem 5(i), (ii), (iv). In particular we show concavity of $e(t)$, which can be interpreted as a bound to the decrease of the ionisation energies. We also derive some of the old results in a new way. Finally we describe a numerical calculation of the Hartree energies, where we find t_c, the critical value of t, as $t_c \simeq 1.21$.

2. Definition of functionals

We begin by making precise the assumptions on the various terms of the functional. The external potential $U(x)$ is assumed to be relative compact with respect to the quantum kinetic energy operator $-\Delta$, when regarded as an operator in $\mathscr{L}^2$. This is true in particular for any electrostatic potential generated by a charge density with finite total charge. (See standard textbooks on mathematical physics, e.g. Reed and Simon (1979).)

As to the exponent p, we demand $1<p\leqslant 2$. (The case $p=1$ leads to a trivial modification of the Hartree equation.) In case $B>0$, we require $\sigma\in\mathscr{L}^p$. In any case, σ has to be an element of $\mathscr{L}^1$ and of the Hilbert space $\mathscr{H}_C$, which arises as the completion of C_0^∞ in the $\|\cdot\|_C$-norm. This norm is diagonalised by the Fourier transform $\sigma\to\tilde{\sigma}$:

$$\|\sigma\|_C=\int|\tilde{\sigma}(k)|^2k^{-2}\,\mathrm{d}^3k. \tag{5}$$

$\mathscr{H}_C$ is thus the space of distributions the Fourier transforms of which are elements of $\mathscr{L}^2(\mathbb{R}^3, k^{-2}\,\mathrm{d}^3k)$. It contains not only functions, but, for example, also surface charge distributions.

We represent two of the terms in $\mathscr{E}_{\mathrm{TFW}}$ by means of their Legendre conjugates. The following representation of the electrostatic repulsion has, in the context of the Hartree equation, first been used by Bazley and Seydel (1974):

$$\|\sigma\|_C^2/2=\sup_{\rho\in\mathscr{H}_C}\{\langle\rho,\sigma\rangle_C-\|\rho\|_C^2/2\}. \tag{6}$$

$\langle\cdot,\cdot\rangle_C$ denotes the inner product in $\mathscr{H}_C$. The supremum is obviously obtained at a unique ρ, namely at $\rho=\sigma$. The analogous representation of the TF kinetic energy is the following:

Let q be such that $1/p+1/q=1$, then

$$p^{-1}\int|\sigma(x)|^p\,\mathrm{d}^3x=\sup_{v\in\mathscr{L}^q}\left\{\int v(x)\sigma(x)\,\mathrm{d}^3x-q^{-1}\int|v(x)|^q\,\mathrm{d}^3x\right\}. \tag{7}$$

Again the supremum is obtained at a unique v, namely at $v=\sigma^{p-1}$.

The remaining terms in $\mathscr{E}_{\mathrm{TFW}}$ are quadratic in $\sigma^{1/2}$, which is an element of $\mathscr{L}^2$. We treat them as expectation values of operators in $\mathscr{L}^2$ and make the following definitions.

Let

$$h_0 = -\Delta + U, \tag{8}$$

for $\rho \in \mathscr{H}_C$ and $v \in \mathscr{L}^q$ set

$$V_\rho(x) = \int |x-y|^{-1}\rho(y)\,\mathrm{d}^3y, \tag{9}$$

$$h_{\rho,v} = h_0 + V_\rho + Bv. \tag{10}$$

Let, moreover,

$$\mathscr{D} = \{\phi \in \mathscr{L}^2 \colon |\phi|^2 \in \mathscr{H}_C \cap \mathscr{L}^p,\ \phi \in \text{form domain of } h_0\},$$

then we define, for $\phi \in \mathscr{D}$, $\rho \in \mathscr{H}_C$, $v \in \mathscr{L}^q$, $t > 0$, the functionals

$$\hat{\mathscr{E}}(\phi, \rho, v) = \langle \phi, h_{\rho,v}\phi\rangle - Bq^{-1}\|v\|_q^q - \tfrac{1}{2}\|\rho\|_C^2, \tag{11}$$

$$\mathscr{E}(t, \rho, v) = \inf \operatorname{spec} h_{\rho,v} - t^{-1}(Bq^{-1}\|v\|_q^q + \tfrac{1}{2}\|\rho\|_C^2). \tag{12}$$

The validity of these definitions is guaranteed by the assumptions on U and the following

Lemma 1. V_ρ and v are relative compact perturbations of h_0 and $\mathscr{D}$ is a core for $h_{\rho,v}$.

Proof. In terms of V_ρ the C-norm of ρ equals $(\int |\nabla V_\rho|^2)^{1/2}$. By Sobolev's inequality, $V_\rho \in \mathscr{L}^6$. Thus both V_ρ and v are in $\mathscr{L}^2 + (\mathscr{L}^\infty)_\varepsilon$. By the Hardy–Littlewood–Sobolev inequality $\mathscr{L}^{6/5} \subset \mathscr{H}_C$, thus $\mathscr{D} \supset \mathscr{L}^p \cap \mathscr{L}^{12/5}$. The rest of the proof is standard (see Reed and Simon (1979), especially example 6 in XIII 4).

Remark. It follows that the essential spectrum of $h_{\rho,v}$ is $[0, \infty)$ and that there exists a unique non-negative ground state wavefunction whenever $h_{\rho,v}$ is not positive.

The various functionals are related by

$$t\mathscr{E}(t, \rho, v) = \inf_{\phi \in \mathscr{D}_t} \hat{\mathscr{E}}(\phi, \rho, v), \tag{13}$$

$$\text{for } \mathscr{D}_t = \{\phi \in \mathscr{D} \colon \|\phi\|_2^2 \leq t\}, \tag{14}$$

$$\mathscr{E}_{\mathrm{TFW}}(\sigma) = \sup_{\rho,v} \hat{\mathscr{E}}(\sigma^{1/2}, \rho, v). \tag{15}$$

It is known that the infimum of $\sup_{\rho,v} \mathscr{E}(\phi, \rho, v)$ is actually attained at a unique ϕ Lieb (1981). Thus

$$E(t) = \inf_{\phi \in \mathscr{D}_t} \sup_{\rho,v} \hat{\mathscr{E}}(\phi, \rho, v). \tag{16}$$

We will eventually show that inf and sup may be exchanged. This implies

$$E(t) = \sup_{\rho,v} t\mathscr{E}(t, \rho, v), \tag{17}$$

and

$$e(t) = \sup_{\rho,v} \mathscr{E}(t, \rho, v). \tag{18}$$

In the sequel we will take (17) and (18) as the definitions of $E(t)$ and $e(t)$. The equivalence to (3), (4) and (16) is shown in § 3 after theorem 4.

3. The functional $\mathscr{E}(t, \rho, v)$

Lemma 2. $\mathscr{E}(t, \rho, v)$ is jointly concave in (t, ρ, v) and jointly weakly upper semicontinuous (WUSC), (in the product of the standard topology on $\mathbb{R}_+$, and the weak topologies on $\mathscr{H}_C$ and $\mathscr{L}^q$). It is strictly concave in (ρ, v).

Proof. $h_{\rho,v}$ is affine in ρ and v. $\inf \operatorname{spec} h_{\rho,v} = \inf_{\phi\in\mathscr{D}_1} \langle\phi, h_{\rho,v}\phi\rangle$, and this infimum of weakly continuous affine functions is WUSC and concave. For $s\in\mathbb{R}$, $t^{-1}|s|^q$ is jointly convex in (t, s). (It is here that the condition $p\leqslant 2$ enters.) Thus for $v\in\mathscr{C}_0$, the functionals $f_x(t, v) = t^{-1}|v(x)|^q$ are jointly convex in (t, v), and so is $\int f_x(t, v)\, d^3x = t^{-1}\|v\|_q^q$. By continuity of the norm, the desired convexity holds on $\mathbb{R}_+\times\mathscr{L}^q$. The same argument applies to $t^{-1}\|\rho\|_C^2$. As norm continuous concave functions, $-t^{-1}\|v\|_q^q$ and $-t^{-1}\|\rho\|_C^2$ are WUSC. The strict concavity in (ρ, v) holds by virtue of the strict convexity of $\|v\|_q^q$ and $\|\rho\|_C^2$.

Theorem 1. For each $t>0$, there exist unique ρ_t and v_t such that $e(t) = \mathscr{E}(t, \rho_t, v_t)$.

Proof. Since $\inf\operatorname{spec} h_{\rho,v}\leqslant 0$ (remark after lemma 1), we have the bound $t\mathscr{E}(t, \rho, v)\leqslant -\|\rho\|_C^2/2 - Bq^{-1}\|v\|_q^q$. Let $E_H = \mathscr{E}(t, 0, 0)$ (the ground state energy of the hydrogen atom). In searching for the supremum of $\mathscr{E}$ at a fixed t we may restrict the domain of $\mathscr{E}$ to the weakly compact sets $\|\rho\|_C^2\leqslant 2t|E_H|$ and $\|v\|_q^q\leqslant B^{-1}t|E_H|$. Now the theorem follows with lemma 2. (For standard results on convex and concave functions and functionals see e.g. Blanchard and Brüning (1982), Rockafellar (1970).) Here we use theorem I.2 of Blanchard and Brüning (1982).)

Definitions.

(a) $h(t) = h_{\rho,v}$ at $\rho = \rho_t$, $v = v_t$

(b) $\mu(t) = \inf\operatorname{spec} h(t)$

(c) $R(t) = \|\rho_t\|_C^2/2 + Bq^{-1}\|v_t\|_q^q$

(d) $r(t) = t^{-2}R(t)$

(e) $\varepsilon = e - rt$

(f) $t_c = \inf\{t\colon \mu(t) = 0\}$, $\rho_c = \rho_{t_c}$, $v_c = v_{t_c}$

(g) ϕ_t is the unique normalised non-negative ground state wavefunction of h_t (for $t<t_c$).

Remarks.

(i) Anticipating the validity of the TFW equation (theorem 3), one has

$$\varepsilon = \langle\phi_t, h_0\phi_t\rangle + t^{-1}B(2-p)p^{-1}\int |\phi_t(x)|^{2p}\, d^3x. \tag{19}$$

(ii) The energies are related by

$$e = \mu - tr \qquad E = \mu t - R \qquad \varepsilon = 2e - \mu. \tag{20a, b, c}$$

(iii) Since $\mu(t_c)=0$ (see theorem 2), the pair (ρ_c, v_c) may be characterised by

$$\|\rho_c\|_C^2/2+Bq^{-1}\|v_c\|_q^q=\inf_{\rho,v}\{\|\rho\|_C^2/2+Bq^{-1}\|v\|_q^q: h_{\rho,v}\geqslant 0\}.$$

(iv) That $t_c>0$, so that the content of this paper is non-void, can be deduced from $\|\rho_t\|_C\to 0$, $\|v_t\|_q\to 0$, as $t\to 0$. The interesting point about t_c is that it is actually strictly larger than one in certain important cases (Lieb 1981).

We gather everything we can deduce about the t-dependence of energies and functions in the following big theorem. While the method of proof seems to be new, not all the results are new. ((ii) to (v) can be found in Lieb (1981).)

Theorem 2.

(i) $e(t)$ is non-positive, non-decreasing and concave,

(ii) $E(t)$ is non-increasing and convex,

(iii) For $t\geqslant t_c$ one has $\mu(t)=0$, $E(t)=E(t_c)$, $\rho_t=\rho_c$, $v_t=v_c$,

(iv) $E(t)$ and $e(t)$ are continuously differentiable,

(v) $E'(t)=\mathrm{d}E(t)/\mathrm{d}t=\mu(t)$, $\mu(t)$ is continuous, non-positive and non-decreasing,

(vi) $e'(t)=r(t)$, $r(t)$ is continuous and non-increasing,

(vii) R is increasing in t. As a function of μ it is the Legendre conjugate of $E(t)$, non-decreasing and convex in μ,

(viii) ε is increasing in t. As a function of $-r$ it is the Legendre conjugate of $-e(t)$, non-increasing and convex in r.

(ix) The derivative of $\mu(t)$ (in the distributional sense) is bounded: $\mu'(t)=E''(t)\leqslant 2r(t)$.

(x) The mapping $t\to\rho_t$ is norm continuous, $t\to v_t$ is weakly continuous.

Proof. (i) and (ii) follow from the respective monotonicity and convexity properties of the functionals $\mathscr{E}$ and $t\mathscr{E}$. We have the fact that the supremum over y of a function $f(x, y)$ which is jointly concave in (x, y) is concave in x.

(iii) Suppose $t>s$ and $\mu(s)=0$. Then $E(t)\geqslant\mathscr{E}(t,\rho_s,v_s)=E(s)$. By continuity of the convex function $E(t)$, also $E(t_c)=E(s)$. $\mu(t_c)=0$ follows from (v). By uniqueness of the minimising ρ and v, and since $\mathscr{E}(t,\rho_t,v_t)$ does not depend on t for $t\geqslant t_c$, it follows that $\rho_t=\rho_c$ and $v_t=v_c$.

(iv) Since $e(t)$ is concave, the right and left derivatives, e_r and e_l, exist and satisfy $e_r(t)\leqslant e_l(t)$. $\mathscr{E}$ is obviously differentiable in t.

Let $s<t<u$. By definition of e:

$$e(u)-e(t)\geqslant\mathscr{E}(u,\rho_t,v_t)-\mathscr{E}(t,\rho_t,v_t)$$

and

$$e(t)-e(s)\leqslant\mathscr{E}(t,\rho_t,v_t)-\mathscr{E}(s,\rho_t,v_t).$$

Thus

$$e_r(t)\geqslant\partial/\partial t\mathscr{E}\geqslant e_l(t).$$

It follows that $e'(t)$ exists and is equal to the partial derivative of $\mathscr{E}$.

(v), (vi), hold, since $r(t)=(\partial/\partial t)\mathscr{E}(t,\rho,v_t)$ and $E'(t)=e(t)-tr(t)=\mu(t)$.

(vii) $R=tE'(t)-E(t)=\sup_{s\geqslant 0}(s\mu-E(s))$ at $\mu=E'(t)$.

$$\mathrm{d}R/\mathrm{d}t=tE''(t)\geqslant 0.$$

(viii) is analogous to (vii): $\varepsilon = \sup_{s\geqslant 0}(-sr + e(s))$.

(ix) By the increase of ε in t, $0 \leqslant (2e-\mu)' = 2r(t) - E''(t)$.

(x) Fix any $s \geqslant 0$. We have seen in the proof of theorem 1 that for $t \leqslant 2s$ the ρ_t and v_t lie in certain weakly compact sets. There exist weak accumulation points $\tilde{v}_s$ and $\tilde{\rho}_s$, when $t \to s$, but since $\mathscr{E}$ is WUSC, $\mathscr{E}(s, \tilde{\rho}_s, \tilde{v}_s) \geqslant \lim_{t\to s} e(t) = e(s)$, so $\tilde{\rho}_s = \rho_s$ and $\tilde{v}_s = v_s$ by the uniqueness property. Since each term in $\mathscr{E}$ is separately WUSC, but $e(t)$ is continuous, the norms $\|\rho_t\|_C$ and $\|v_t\|_q$ are continuous functions of t. In a Hilbert space, a weakly continuous curve with continuous norm is norm continuous.

Remarks.

(i) The increase of $e(t)$ follows also from the convexity of $E(t)$ and form $E(0) = 0$.

(ii) The convexity of $E(t)$ mimics the unproven conjectured monotonicity of the ionisation energy for finite quantum Coulomb systems (Simon 1984). Interpreting the concavity of $e(t)$ in a similar way, it would mean a bound in the opposite direction, saying that the ionisation energies cannot decrease too fast. Part (ix) is the explicit statement of this bound.

(iii) The increase of ε in t is analogous to a certain monotonicity theorem in perturbation theory, for $B = 0$ or $p = 2$. In the case of the Hartree equation it can be considered as the limiting form of this perturbation theoretic result.

Theorem 3.
For $t < t_c$, ϕ_t, ρ_t and v_t solve the TFW equation

$$h(t)\phi_t = \mu(t)\phi_t \qquad \rho_t(x) = v_t(x)^{q-1} = t\phi_t^2(x) \qquad \|\phi_t\|_2 = 1. \tag{22a, b, c}$$

Proof. Equations (a) and (c) are just the definitions of $\mu(t)$ and ϕ_t. Differentiating $\hat{\mathscr{E}}(t, \rho_t + \lambda\rho, v_t + \mu v)$ with respect to λ and μ and using a theorem from analytic perturbation theory (the Feynman Hellman theorem) (Read and Simon 1979), yields (b)). (We remark that $\rho = \phi^2 \in \mathscr{H}_C$ implies $\rho(x) = \phi^2(x)$ almost everywhere.)

A uniqueness theorem for positive solutions of the TFW equation (Reeken 1970, Lieb 1981), shows that our solutions also minimise the TFW functional (1). This is also affirmed by the following theorem.

Theorem 4.

$$\min_{\phi\in\mathscr{D}_t}\max_{\rho,v} \hat{\mathscr{E}}(\phi, \rho, v) = \max_{\rho,v}\min_{\phi\in\mathscr{D}_t} \hat{\mathscr{E}}(\phi, \rho, v) \qquad \text{for } t < t_c.$$

Proof. The domain of $\hat{\mathscr{E}}$ may on both sides be restricted to positive functions. We may, therefore, consider $\hat{\mathscr{E}}(\sigma^{1/2}, \rho, v)$, for $\sigma \geqslant 0$, $\sigma \in \mathscr{L}^1 \cap \mathscr{L}^p \cap \mathscr{H}_C$, $\|\sigma\|_1 = t$, which is a convex set. This functional is convex in σ (Lieb 1981) and concave in (ρ, v). Thus the triple $(\sigma_t = \phi_t^2, \rho_t, v_t)$ is a saddle point and the interchange of min and max is allowed (Rockafellar 1970).

Remark. It is not difficult to establish weak lower semicontinuity of $\hat{\mathscr{E}}$ in ϕ and thus extend this theorem to $t \geqslant t_c$. But we have proven just enough to guarantee the equivalence of the two formulae (16) and (17) for $E(t)$. For $E(t)$ has the property that $E(t) = \lim_{s\nearrow t_c} E(s)$ for $t \geqslant t_c$ by (ii) and (iii) of theorem 2. But the right-hand side of (16) has the same property (theorem 7.8 of Lieb (1981)).

Theorem 5. (The virial theorem and related results).

Suppose $U(x) = -Z/|x|$. Let

$$K = A \int |\nabla \sigma_t^{1/2}(x)|^2 \, d^3x, \qquad \bar{K} = Bp^{-1} \|\sigma_t\|_p^p,$$

$$A = -Z \int \sigma_t(x)/|x| \, d^3x, \qquad \bar{R} = \|\sigma_t\|_C^2/2.$$

Then the following relations hold:

(i) $2K + 3(p-1)\bar{K} + A + \bar{R} = 0$

(ii) $K + (3p-4)\bar{K} + E = 0$

(iii) $\mu t = K + p\bar{K} + A + 2\bar{R}$

(iv) if $B = 0$ and $t = t_c$, then $-E : K : \bar{R} : -A = 1:1:1:3$.

Proof.

(i) follows from the usual scaling argument: consider $\sigma_{t,\lambda} = \lambda^3 \sigma_t(\lambda x)$. $(d/d\lambda)\mathscr{E}_{TFW}(\sigma_{t,\lambda})_{\lambda=0} = 0$ gives the equation.

(ii) follows from (i) and from $E = K + \bar{K} + A + \bar{R}$.

(iii) is the equation $\mu t = E + R$.

(iv) follows from (i) and (iii).

4. Numerical evaluation of Hartree energies

Here $B = 0$ and with the help of a suitable scale transformation $(x \to Ax)$, we can set $A = 1$. Since the solution we are looking for is spherically symmetric, we can get

$$\chi_t(r) = 2\pi^{1/2} t^{1/2} r\phi_t(x) \qquad \text{at } r = |x|. \tag{22}$$

The $\mathscr{L}^2$-norms of χ and $t^{1/2}\phi$ are equal:

$$\int_0^\infty \chi_t(r)^2 \, dr = t. \tag{23}$$

The Hartree equation for χ_t is

$$(-d^2/dr^2 - r^{-1} + V_t(r) - \mu(t))\chi_t = 0 \tag{24}$$

with

$$V_t(|x|) = t \int |x-y|^{-1} \phi_t^2(y) \, d^3y.$$

With the help of Gauss' law this can be transformed to

$$V_t(r) = V_t(0) + \int_0^r (r^{-1} - s^{-1}) \chi_t^2(s) \, ds. \tag{25}$$

The Hartree equation is thus written as the following integro-differential equation:

$$(-d^2/dr^2 - r^{-1} - I(r) + r^{-1}J(r) - \eta)\chi = 0 \tag{26a}$$

$$I(r) = \int_0^r s^{-1}\chi^2(s) \, ds \qquad J(r) = \int_0^r \chi^2(s) \, ds \tag{26b, c}$$

$$\eta = \mu - V(0).$$

In this form it can be treated in much the same way as the ordinary Schrödinger equation. One starts to integrate from $r=0$. There $\chi=0$, but one has to choose η and $\chi'(0)$. In the generic case $\chi(r)$ will soon go through zero or start to diverge ($\chi'(r)>0$ and $\chi''(r)>0$). To find a better $\chi(r)$, one chooses a larger $\chi'(0)$ in the first case, a smaller one in the second case. If η is in the appropriate range (between -0.25 and approximately -0.373), one will in this way approximate an exponentially decreasing positive solution $\chi(r)$. The physically interesting parameters are now determined by

$$t=J(\infty), \qquad V(0)=I(\infty), \qquad \mu(t)=\eta+I(\infty). \qquad (27a, b, c)$$

All the other energies require additional integration. We have chosen to calculate

$$K(t)=\int_0^\infty (\chi'(r))^2\,\mathrm{d}r, \qquad (28)$$

and use $E=-K$, $e=E/t$, $\varepsilon=2e-\mu$, $R=K+t\mu$, $r=R/t^2$.

Starting with a different value of η yields a different value of t. The boundary cases $\eta=-0.25$ and $\eta\sim-0.373$ correspond to the hydrogen atom ($t=0$, $\mu=e=\varepsilon=\eta$) and to the critical solution with $t_c\sim1.21$ and $\mu(t_c)=0$.

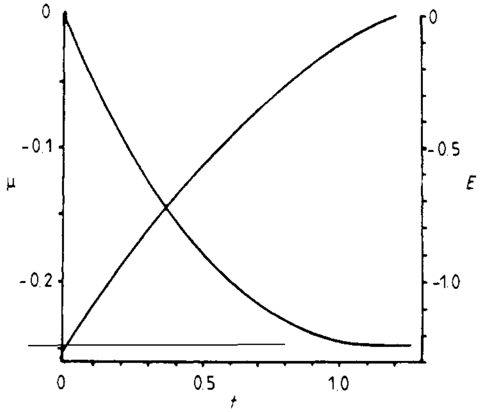

Figure 1. E and μ as functions of t.

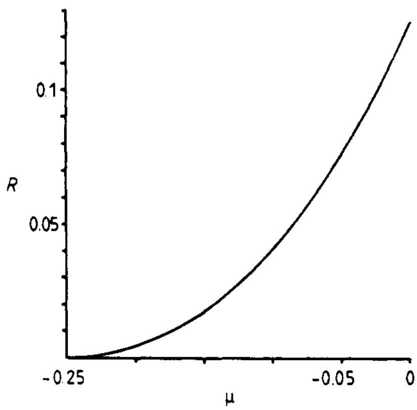

Figure 2. R as a function of μ.

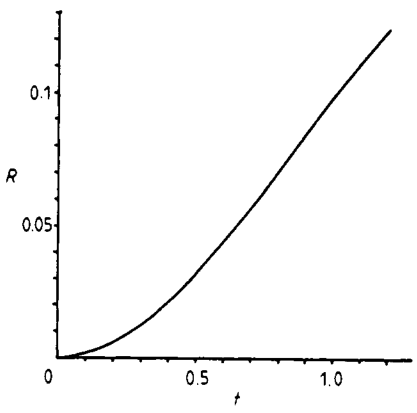

Figure 3. R as a function of t.

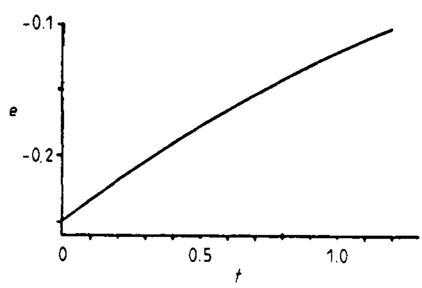

Figure 4. e as a function of t.

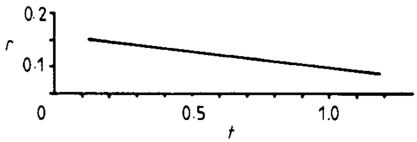

Figure 5. r as a function of t.

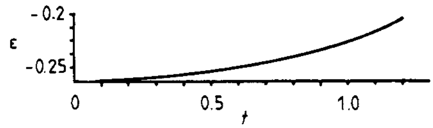

Figure 6. ε as a function of t.

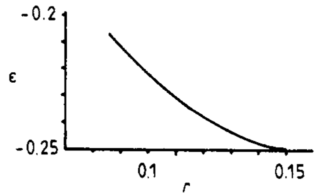

Figure 7. ε as a function of r.

Choosing $\eta > -0.25$ yields nothing other than oscillating solutions. For $\eta < -0.373$ the algorithm described above leads to a χ which goes first through a maximum as any other solution, then it falls off until it reaches a point r_1, where $\chi'(r_1) = \chi''(r_1) = 0$. There it does not start to diverge, rather it falls off again until it reaches zero at r_2. In this way one gets a solution for a finite volume, with Dirichlet boundary conditions if one stops at r_2, with Neumann boundary conditions if one stops at r_1. In both cases $t > t_c$ and $\mu(t) > 0$ is a seemingly smooth continuation of the function $\mu(t)$. The zero of this extended $\mu(t)$ determines the critical value t_c.

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