A Derivation of the $Z \to \infty$ Limit for Atoms\textsuperscript{*})

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Upper and lower bounds are derived for the ground-state energy of neutral atoms which for $Z \to \infty$ both involve the limits of exact Greens functions with one-body potentials. The limits of both bounds are shown to coincide with the Thomas–Fermi ground-state energy.

\section{Introduction}

A very remarkable property of atoms is that in the limit $Z \to \infty$, the Thomas–Fermi energy\textsuperscript{1,2,3}) becomes exact\textsuperscript{4,5,6}) Unfortunately, the very ingenious proofs of this beautiful result are somewhat complex. We have strived in developing a relatively easier, but rather formal, derivation of this fundamental result for neutral atoms by using, in the process, the Greens function corresponding to the Thomas–Fermi potential. The derivation rests on the fact that elementary scaling properties of integrals of the Greens function allow one readily to consider the $Z \to \infty$ limit with no difficulty. The basic idea is that integrals of the Greens function for coincident space points involved in the analysis have particularly simple power law behaviour for large $Z$. This is spelled out in the text.

For the Hamiltonian of neutral atoms we choose

$$H = \sum_{\alpha=1}^{Z} \left( \frac{p_{\alpha}^2}{2m} - \frac{Ze_{\alpha}^2}{r_{\alpha}} \right) + \sum_{\alpha<\beta}^{Z} \frac{e_{\alpha}^2}{|r_{\alpha} - r_{\beta}|}. \quad (1)$$

We derive upper and lower bounds on the exact ground-state energy of (1), which for $Z \to \infty$ are the limits of expressions involving integrals of the exact Greens functions with one-body potentials. The limits of both bounds are shown to coincide with the ground-state Thomas–Fermi energy, thus establishing the result.

\section{The upper bound}

We consider first the seemingly unrelated problem of a one-body potential with Hamiltonian

$$h = \frac{p^2}{2m} + V(r) \quad (2)$$

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where $V(\mathbf{r})$ is the Thomas–Fermi potential

$$V(\mathbf{r}) = -\frac{Ze^2}{r} + e^2 \int d^3 \mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = Z^{4/3} v(\mathbf{R})$$

$$= -\frac{\hbar^2}{2m} \left(3\pi^2\right)^{2/3} Z^{4/3} (\rho_{\text{TF}}(\mathbf{R}))^{2/3}, \quad \mathbf{r} = \frac{\mathbf{R}}{Z^{1/3}};$$

and $n(\mathbf{r}) = Z^2 \rho_{\text{TF}}(\mathbf{R})$ is the Thomas–Fermi density normalized as

$$\int d^3 \mathbf{r} n(\mathbf{r}) = Z.$$

The Greens function corresponding to (2) satisfies the equation

$$\left[ -i \frac{\partial}{\partial \tau} - \frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] G_{\pm} (\mathbf{r}, \mathbf{r}'0) = \delta^3(\mathbf{r} - \mathbf{r}')\delta(t),$$

where, with appropriate boundary conditions,

$$G_{\pm} (\mathbf{r}, \mathbf{r}'0) = \pm \left(\frac{i}{\hbar}\right) \Theta(\mp t) G_0 (\mathbf{r}, \mathbf{r}'0; V), \quad t = \frac{\tau}{\hbar}.$$ 

We write

$$G_0 (\mathbf{r}, \mathbf{r}'0; V) = \int \frac{d^3 \mathbf{k}}{(2\pi)^3} e^{i \mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')} \exp \left[ -i \left( \frac{\hbar^2 k^2}{2m} \tau + U(\mathbf{r}, \tau, \mathbf{k}) \right) \right].$$

We readily see that $U$ satisfies the equation

$$- \frac{\partial U}{\partial \tau} + V - \frac{\hbar^2}{m} \mathbf{k} \cdot \nabla U + \frac{\hbar^2}{2m} (\nabla U)^2 + i \frac{\hbar^2}{2m} \nabla^2 U = 0,$$

with the boundary condition $U \big|_{\tau=0} = 0$. We are particularly interested in the integral

$$\int d^3 \mathbf{r} \ G_0 (\mathbf{r}, \mathbf{r}'0; V),$$

where $\exp [i \mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')]$ in (7) becomes simply replaced by 1. Under a scaling we have $\mathbf{r} = \mathbf{R}/Z^{1/3}, \ V(\mathbf{r}) = Z^{4/3} v(\mathbf{R})$, where $v(\mathbf{R})$ is independent of $Z$. Accordingly, to study the large $Z$ behaviour, we carry out the change of variables $\mathbf{r} \to \mathbf{R}$ and simultaneously substitute $\tau = T/Z^{4/3}$. Also, with the change of variables $\mathbf{k} \to \mathbf{K}, \ \mathbf{k} = Z^{2/3} \mathbf{K}$, the product $k^2 \tau = K^2 T$ in (7) remains invariant. With these new variables, (8) becomes

$$- \frac{\partial U}{\partial T} + v - \frac{\hbar^2}{mZ^{1/3}} \mathbf{K} \cdot \nabla_R U + \frac{\hbar^2}{2mZ^{2/3}} (\nabla_R U)^2 + i \frac{\hbar^2}{2mZ^{2/3}} \nabla^2_R U = 0.$$

Let $\lim_{Z \to \infty} U = U_\infty$. Then (10) collapses to $-\partial U_\infty/\partial t + v = 0$, whose solution is $U_\infty = vT$. Hence for $Z \to \infty$, the expression in (9) becomes simply scaled by
expression for (9) as before, with an overall scaling by \( Z \). The latter, under the subsequent change of variables \( \mathbf{K} \rightarrow Z^{1/3} \mathbf{K} \), leads to \( [\hbar^2 \mathbf{K}^2 T/2mZ^{2/3} + vT + \mathcal{O}(Z^{-2/3})] \), giving the same expression for (9) as before, with an overall scaling by \( Z \).

Accordingly, we have the following limits for large \( Z \), as readily verified upon substitution of \( vT \) for \( U \), \( Z \rightarrow \infty \):

\[
\int d^3r \frac{2}{(2\pi i)^3} \int_{-\infty}^{\infty} \frac{d\tau}{\tau - i\epsilon} G_0(\mathbf{r}\tau, \mathbf{r}0; V) \rightarrow Z \int d^3\mathbf{R} \rho_{\text{TF}}(\mathbf{R}) \equiv Z, \tag{11a}
\]

\[
Z^{-7/3} \int d^3r \frac{2}{(2\pi i)^3} \int_{-\infty}^{\infty} \frac{d\tau}{\tau - i\epsilon} \frac{\partial}{\partial \tau} G_0(\mathbf{r}\tau, \mathbf{r}0; V)
\rightarrow 2 \int d^3\mathbf{R} \int d^3\mathbf{K} \left[ \frac{\hbar^2 \mathbf{K}^2}{2m} + v(\mathbf{R}) \right] \Theta \left( \sqrt{\frac{-2mv(\mathbf{R})}{\hbar^2} - |\mathbf{K}|} \right)
\]

\[
= (3\pi^2)^{5/3} \frac{\hbar^2}{10\pi^2m} \int d^3\mathbf{R} \left( \rho_{\text{TF}}(\mathbf{R}) \right)^{5/3} - e^2 \int d^3\mathbf{R} \frac{\rho_{\text{TF}}(\mathbf{R})}{R}
\]

\[
+ e^2 \int d^3\mathbf{R} \int d^3\mathbf{R}' \rho_{\text{TF}}(\mathbf{R}) \frac{1}{|\mathbf{R} - \mathbf{R}'|} \rho_{\text{TF}}(\mathbf{R}'). \tag{11b}
\]

Here, the factor 2 multiplying the \( \tau \)-integrals is to account for spin. The \( \tau \)-integrals project out the negative spectrum of \( h \).

Equation (11a) in particular is of fundamental importance. It states that for large \( Z \), the Hamiltonian \( h \), allowing for spin, has \( Z \) (orthonormal) eigenvectors corresponding to its negative spectrum. Let \( g_1(\mathbf{r}, \sigma), \ldots, g_Z(\mathbf{r}, \sigma) \) denote these eigenvectors for large \( Z \). Define the determinantal (anti-symmetric) function

\[
\phi_Z(\mathbf{r}_1\sigma_1, \ldots, \mathbf{r}_Z\sigma_Z) = \frac{1}{\sqrt{Z!}} \det \left[ g_\alpha(\mathbf{r}_\beta, \sigma_\beta) \right]. \tag{12}
\]

Since such an anti-symmetric function does not necessarily coincide with the ground-state function of the Hamiltonian \( H \) in (1) in question, the expectation value \( \langle \phi_Z | H | \phi_Z \rangle \) with respect to \( \phi_Z \) in (12) can only overestimate the exact ground-state energy \( E_Z \) of \( H \), or at best be equal to it.

We rewrite the Hamiltonian in (1) equivalently as

\[
H = \sum_{\alpha=1}^{Z} h_\alpha + \left( \sum_{\alpha<\beta} \frac{e^2}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} - e^2 \sum_{\alpha=1}^{Z} \int d^3\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}_\alpha - \mathbf{r}'|} \right), \tag{13}
\]

where \( h_\alpha \) is defined in (2) with variables \( \mathbf{r}_\alpha, \mathbf{p}_\alpha \).

Accordingly,

\[
\lim_{Z \rightarrow \infty} Z^{-7/3} E_Z \leq \lim_{Z \rightarrow \infty} Z^{-7/3} \langle \phi_Z | H | \phi_Z \rangle
\]

\[
= \lim_{Z \rightarrow \infty} Z^{-7/3} \sum_{\alpha=1}^{Z} \langle g_\alpha | h_\alpha | g_\alpha \rangle + \lim_{Z \rightarrow \infty} Z^{-7/3} F_Z, \tag{14}
\]
where

\[ F_Z = -e^2 \sum_{\sigma} \int \frac{d^3r d^3r'}{|r - r'|} n_Z(r\sigma, r\sigma) n(r') \]
\[ + \frac{e^2}{2} \sum_{\sigma, \sigma'} \int \frac{d^3r d^3r'}{|r - r'|} \left[ n_Z(r\sigma, r\sigma) n_Z(r'\sigma', r'\sigma') - |n_Z(r\sigma, r'\sigma')|^2 \right], \tag{15} \]

or

\[ F_Z \leq -e^2 \int \frac{d^3r d^3r'}{|r - r'|} \left[ n(r') \left( \sum_{\sigma} n_Z(r\sigma, r\sigma) \right) \right. \]
\[ - \frac{1}{2} \left( \sum_{\sigma} n_Z(r\sigma, r\sigma) \right) \left( \sum_{\sigma'} n_Z(r'\sigma', r'\sigma') \right) \]. \tag{17} \]

However, we also have

\[ \lim_{Z \to \infty} Z^{-2} \sum_{\sigma} n_Z(r\sigma, r\sigma) = \lim_{Z \to \infty} Z^{-2} \frac{2}{2\pi i} \int_{-\infty}^{\infty} \frac{d\tau}{\tau - i\epsilon} G_0(\tau r, \tau r'; V) \equiv \rho_{TF}(R), \tag{18} \]

\[ \lim_{Z \to \infty} Z^{-7/3} \sum_{\alpha=1}^{Z} \langle g_{\alpha} | h_{\alpha} | g_{\alpha} \rangle = \lim_{Z \to \infty} Z^{-7/3} 2 \sum_{\lambda < 0} \lambda \]
\[ = \lim_{Z \to \infty} Z^{-7/3} \int d^3r \frac{2}{2\pi i} \int_{-\infty}^{\infty} \frac{d\tau}{\tau - i\epsilon} \]
\[ \times i \frac{\partial}{\partial \tau} G_0(\tau r, \tau r'; V), \tag{19} \]

where \( \sum_{\lambda < 0} \lambda \) is a sum over all the negative eigenvalues of \( h \) in (2), allowing for multiplicity but not spin degeneracy. The factor 2 takes the latter into account.

From (14)–(19) and (11b), we finally have

\[ \lim_{Z \to \infty} Z^{-7/3} E_Z \leq \frac{(3\pi^2)^{5/3} \hbar^2}{10\pi^2 m} \int d^3R \left( \rho_{TF}(R) \right)^{5/3} - e^2 \int d^3R \frac{\rho_{TF}(R)}{R} \]
\[ + \frac{e^2}{2} \int d^3R d^3R' \rho_{TF}(R) \frac{1}{|R - R'|} \rho_{TF}(R'), \tag{20} \]

and the right-hand side is the coefficient of \( Z^{7/3} \) of the ground-state Thomas–Fermi energy.
§3. The lower bound

Given any arbitrary real and positive function $\rho_Z(r)$, we use the following elementary text-book bound\textsuperscript{20}:

$$
\sum_{\alpha<\beta}^{Z} \frac{1}{|r_\alpha - r_\beta|} \geq \sum_{\alpha=1}^{Z} \int d^3r \frac{\rho_Z(r)}{|r - r_\alpha|} - \frac{1}{2} \int d^3r d^3r' \rho_Z(r) \frac{1}{|r - r'|} \rho_Z(r')
$$

$$
- \frac{3}{2} \pi^{1/3} Z^{2/3} \left[ \int d^3r \ (\rho_Z(r))^2 \right]^{1/3}.
$$

(21)

Here the real function $\rho_Z(r)$ may be chosen to be positive and is otherwise arbitrary (i.e., may be chosen at will) to the extent that the integrals on the right-hand side of (21) exist. We conveniently choose it in such a way that $\rho_Z(r) \rightarrow Z^2 \rho_{\text{TF}}(r)$ for $Z \rightarrow \infty$, which will then coincide with $n(r)$ used above in (3). Consider the Hamiltonian $h' = p^2/2m + V'$, where

$$
V'(r) = -\frac{Ze^2}{r} + e^2 \int d^3r' \frac{\rho_Z(r')}{|r - r'|}.
$$

(22)

With $\rho_Z(r)$ conveniently chosen, $V'(r)$ may be chosen to be a locally square integrable function satisfying $V'(r) \rightarrow 0$ for $r \rightarrow \infty$. Let $\psi$ be a normalized antisymmetric function in $(r_1, \sigma_1, \ldots, r_z, \sigma_z)$. Then (21) implies that

$$
\langle \psi | H | \psi \rangle \geq \left\langle \psi \left| \sum_{\alpha} h'_\alpha \right| \psi \right\rangle - \frac{e^2}{2} \int d^3r d^3r' \rho_Z(r) \frac{1}{|r - r'|} \rho_Z(r')
$$

$$
- \frac{3}{2} \pi^{1/3} Z^{2/3} e^2 \left[ \int d^3r \ (\rho_Z(r))^2 \right]^{1/3}.
$$

(23)

Consider the lowest energy $E$ of the Hamiltonian $\sum_{\alpha} h'_\alpha$. The Pauli exclusion principle comes to the rescue here\textsuperscript{13}. Concerning the Hamiltonian $\sum_{\alpha} h'_\alpha$, the Z “non-interacting” electrons (although each interacts with an external potential $V'$) can be put, according to the Pauli exclusion principle, in the lowest energy levels of $\sum_{\alpha} h'_\alpha$ (allowing for spin degeneracy) if $Z$ is less than the number of such available levels. If $Z$ is larger, then the remaining free electrons should have arbitrarily small kinetic energies to define the lowest energy of $\sum_{\alpha} h'_\alpha$. In either case, $E \geq 2 \sum_{\lambda<0} \lambda$, where $\sum_{\lambda<0} \lambda$, defined as above, is now applied to $h'$. Accordingly,

$$
\lim_{Z \rightarrow \infty} Z^{-7/3} \langle \psi | H | \psi \rangle \geq \lim_{Z \rightarrow \infty} K_Z,
$$

(24)

where

$$
K_Z = Z^{-7/3} \int d^3r \frac{2}{2\pi i} \int_{-\infty}^{\infty} \frac{d\tau}{\tau - i\varepsilon} \frac{i}{\partial\tau} G_0(r\tau, r0; V')
$$

$$
- Z^{-7/3} \frac{e^2}{2} \int d^3r d^3r' \rho_Z(r) \frac{1}{|r - r'|} \rho_Z(r')
$$

$$
- \frac{3}{2} \pi^{1/3} Z^{-5/3} e^2 \left[ \int d^3r \ (\rho_Z(r))^2 \right]^{1/3}.
$$

(25)
and \( G_0(\mathbf{r}_1, \mathbf{r}_0; V') \) is defined as above. Also here we have used the equality on the extreme right-hand side of \( (19) \). Since the right-hand side of the inequality \( (24) \) is independent of \( \psi \), this inequality holds with \( \psi \) corresponding to the ground-state function of \( H \) as well, i.e., with \( \langle \psi | H | \psi \rangle \) corresponding to

\[
\min_{\psi} \langle \psi | H | \psi \rangle = E_Z. \tag{26}
\]

To the extent that \( \rho \) is arbitrary, we choose it conveniently as

\[
\rho_Z(\mathbf{r}) = Z^2 \rho_{\text{TF}}(R) \sqrt{1 - e^{-Z \alpha R}}, \tag{27}
\]

where \( \alpha > 0 \) is an arbitrary scale parameter. We note that \( \rho_{\text{TF}}(R) \sim R^{-3/2} \) for \( R \to 0 \), and that \( \rho_{\text{TF}}(R) \sim R^{-6} \) for \( R \to \infty \). The factor \( \sqrt{1 - \exp(-Z \alpha R)} \) ensures the integrability of the last integral on the right-hand side of \( (25) \). We estimate the latter for \( Z \to \infty \) as

\[
\frac{1}{Z^{2/3}} \left[ \int d^3 R \left( 1 - e^{-Z \alpha R} \right)^{1/3} \rho_{\text{TF}}^2(R) \right]^{1/3} \leq \left[ \int_{\alpha R \leq 1/Z} d^3 R \frac{\alpha}{Z} R \rho_{\text{TF}}^2(R) \right. + \left. \frac{1 - e^{-Z}}{Z^2} \int_{1/Z < R > 1/Z} d^3 R \rho_{\text{TF}}^2(R) \right]^{1/3} + \frac{1}{Z^2} \int_{\alpha R \geq 1} d^3 R \rho_{\text{TF}}^2(R). \tag{28}
\]

The second integral on the right-hand side is at worst logarithmic in \( Z \). Hence the last term on the right-hand side of \( (25) \) vanishes for \( Z \to \infty \). Since \( - (1 - e^{-Z \alpha R}) \geq -1 \), the second term (with the minus sign) on the right-hand side of \( (25) \) is bounded below by

\[
- \frac{e^2}{2} \int d^3 R d^3 R' \rho_{\text{TF}}(R) \rho_{\text{TF}}(R') \frac{1}{|R - R'|}. \tag{29}
\]

Finally, we note that since \( 1 - e^{-Z \alpha R} \to 1 \) for \( Z \to \infty \), and with \( V' \equiv Z^{4/3} v'_Z \) and \( \lim_{Z \to \infty} v'_Z \equiv v(R) \), the limit of the first expression on the right-hand side of \( (25) \) coincides with that in \( (11) \) for \( Z \to \infty \). All told, we see that the lower bound in \( (24) \) coincides with the upper bound in \( (20) \). This completes our demonstration.

In a future report, we will investigate to what extent this analysis may be extended to other interactions.

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