Temperature dependence of the Slater sum: Generalization of the one-dimensional Thomas-Fermi theory

C. Amovilli and N. H. March
Department of Theoretical Chemistry, University of Oxford, 5 South Parks Road, Oxford OX1 3UB, England
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The one-dimensional equation of motion for the canonical or Bloch density matrix is solved by the method of separation of variables for independent particles moving in a potential $V(x)$. The solution is exact when third and higher derivatives of $V(x)$ are zero, embracing thereby the examples of (a) harmonic potentials and (b) a constant electric field of arbitrary strength. The form of the Slater sum obtained involves then two functions of temperature only, to be determined. One obvious relation between these two functions is via the partition function. A further relation comes from the orthonormality of the wave functions appearing in the Slater sum: the analog of idempotency for the ground-state Dirac density matrix. These two conditions again are shown to lead back to the exact result for harmonic potentials. The results presented generalize the one-dimensional Thomas-Fermi theory to apply to a temperature range that is significantly wider than for the original method.

I. INTRODUCTION

A good deal of attention has been given to the solution of the Bloch equation

$$\hat{H}_{\mathbf{r}}C(\mathbf{r},\mathbf{r}_0,\beta)=-\frac{\partial C}{\partial\beta}\quad[C(\mathbf{r},\mathbf{r}_0,0)=\delta(\mathbf{r}-\mathbf{r})_0] \tag{1.1}$$

for the canonical density matrix

$$C(\mathbf{r},\mathbf{r}_0,\beta)=\sum_i \psi_i(\mathbf{r})\psi_i^*(\mathbf{r}_0)\exp(-\beta\varepsilon_i)\ . \tag{1.2}$$

Here, ψ_i and ε_i denote the eigenfunctions and eigenvalues of the one-body Hamiltonian

$$\hat{H}_{\mathbf{r}}=-\tfrac{1}{2}\nabla_{\mathbf{r}}^2+V(\mathbf{r})\ . \tag{1.3}$$

One can mention the entire perturbation series [1] generated by starting from the plane-wave result

$$C_0(\mathbf{r},\mathbf{r}_0,\beta)=\frac{1}{(2\pi\beta)^{3/2}}\exp\left[-\frac{|\mathbf{r}-\mathbf{r}_0|^2}{2\beta}\right] \tag{1.4}$$

and the nonperturbative, but approximate, work of Hilton, March, and Curtis [2], who write

$$C(\mathbf{r},\mathbf{r}_0,\beta)=C_0(\mathbf{r},\mathbf{r}_0,\beta)\exp[-\beta U(\mathbf{r},\mathbf{r}_0,\beta)]\ , \tag{1.5}$$

with U the so-called effective potential matrix. Their work gave U to first order in V analytically, but to obtain higher-order results numerical iteration of the integral form of Eq. (1.1) had to be carried out. Taking the diagonal element $\mathbf{r}_0=\mathbf{r}$ in Eq. (1.5) and using $U(\mathbf{r},\mathbf{r},\beta)\simeq V(\mathbf{r})$ leads back to the Thomas-Fermi (TF) approximation:

$$C_{\mathrm{TF}}(\mathbf{r},\beta)=C_0(\beta)\exp[-\beta V(\mathbf{r})]\ . \tag{1.6}$$

Equation (1.6) provides the motivation for the development given below. However, it has so far proved necessary to work in one dimension to make substantial analytical progress. It is relevant to mention at this point that March and Murray [3] have shown that knowledge of the "nondegenerate" density $C(\mathbf{r},\beta)$ is indeed sufficient to determine the ground-state density $\rho(\mathbf{r},E)$, as well as the density given by the Fermi-Dirac statistic at elevated temperature. Thus methods for the calculation of the Slater sum are of considerable interest; applications that might be cited being confined atoms in low-density plasmas, produced by intense electric fields due to laser irradiation [4,5].

II. GENERALIZED TF APPROXIMATION IN ONE DIMENSION

Using Eq. (1.1) with $\mathbf{r}\to\mathbf{r}_0$ and then subtracting the result from the original equation yields in one dimension

$$\frac{\partial^2 C(x,x_0,\beta)}{\partial x^2}-\frac{\partial^2 C(x,x_0,\beta)}{\partial x_0^2}=2[V(x)-V(x_0)]C(x,x_0,\beta)\ . \tag{2.1}$$

Following March and Young [6], who, however, considered only the ground-state Dirac density matrix, not $C(x,x_0,\beta)$, we now introduce sum and difference coordinates

$$\xi=\frac{x+x_0}{2},\quad \eta=\frac{x-x_0}{2} \tag{2.2}$$

to find

$$\frac{\partial^2 C}{\partial\xi\partial\eta}=2[V(\xi+\eta)-V(\xi-\eta)]C\ . \tag{2.3}$$

Expanding around the point $\eta=0$ one obtains almost immediately

$$\frac{\partial^2 C}{\partial\xi\partial\eta}=4\eta V'(\xi)C\ , \tag{2.4}$$

which corresponds to neglect of third and higher derivatives of V. This equation has a separable solution of the form

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$$C(\xi,\eta,\beta)=G(\xi,\beta)H(\eta,\beta) \tag{2.5}$$

and introducing the "separation constant" $K(\beta)$ it readily follows that

$$C(\xi,\eta,\beta)=A(\beta)\exp\left[-\frac{2\eta^2}{K(\beta)}\right]\exp[-K(\beta)V(\xi)] \ . \tag{2.6}$$

One sees immediately that on the diagonal ($\eta=0$) Eq. (2.6) contains the TF result (1.6) written now in one dimension provided:

$$\begin{aligned} &A(\beta)\to C_0(\beta)=(2\pi\beta)^{-1/2} \ , \\ &K(\beta)\to\beta \ . \end{aligned} \tag{2.7}$$

This form (2.6) is the proposed generalization of the TF approximation for the one-dimensional canonical density matrix. The separation function $K(\beta)$, to be discussed in Secs. III and IV, is the important new component of the theory, the form (2.7) being the TF limit. Let us immediately turn to present two illustrative examples.

III. EXAMPLES OF HARMONIC POTENTIAL AND OF CONSTANT ELECTRIC FIELD

Let us now see how the two functions of temperature $A(\beta)$ and $K(\beta)$ can be determined for (a) a harmonic potential and (b) a constant electric field E of arbitrary magnitude, represented by the potential energy $-Ex$.

The starting point is the diagonal form of the Bloch equation given by March and Murray [3]. Applying their Eq. (4.7) for the $l=0$ readily yields the one-dimensional equation (see also the later studies in Refs. [7] and [8]):

$$\frac{1}{8}\frac{\partial^3 C}{\partial x^3}-\frac{\partial^2 C}{\partial x\partial\beta}-V\frac{\partial C}{\partial x}-\frac{1}{2}\frac{\partial V}{\partial x}C=0 \quad [C=C(x,x,\beta)] \ . \tag{3.1}$$

Substituting C in this equation yields

$$-KV'''+3K^2V''V'-K^3(V')^3+4\left[2K'+2K\frac{A'}{A}-1\right]V' -8K(K'-1)V'V=0 \ . \tag{3.2}$$

A. Harmonic oscillator

Putting $V(x)=\frac{1}{2}\omega^2x^2$ we can equate separately coefficients of x^3 and of x to zero to find

$$K'=1-\tfrac{1}{4}K^2\omega^2 \tag{3.3}$$

and

$$\frac{A'}{A}=-\frac{1}{2K}(1+\tfrac{1}{4}K^2\omega^2) \ . \tag{3.4}$$

B. Constant electric field

Setting $V(x)=-Ex$, and using precisely the same procedure, one finds

$$K'=1 \ , \tag{3.5}$$

$$\frac{A'}{A}=-\frac{1}{2K}+\frac{K^2E^2}{8} \ . \tag{3.6}$$

The desired integral of the first equation is simply the TF limit of small β, namely $K(\beta)=\beta$, and substituting this into the equation for A'/A this can be integrated to yield

$$A(\beta)=\frac{1}{(2\pi\beta)^{1/2}}\exp\left[\frac{\beta^3E^2}{24}\right] \ . \tag{3.7}$$

The result for the constant electric field appears first, to our knowledge, in the work of Jannussis [9]; see also Harris and Cina [10].

IV. SLATER SUM RELATED TO THE PARTITION FUNCTION

Having clarified the way the form for the Slater sum is exactly calculable for the two examples above where third and higher derivatives of V are zero, we must now inquire how, in a more general context, the now approximate form (2.6) can be useful. We note first that, though the Slater sum may not be known, the knowledge of the (exact) partition function for a given potential $V(x)$ can be employed first to relate $A(\beta)$ and $K(\beta)$ for a general one-dimensional potential $V(x)$.

Thus, starting from the approximate form (2.6), one has evidently

$$Z(\beta)=A(\beta)\int_{-\infty}^{\infty}dx\,\exp[-K(\beta)V(x)] \ . \tag{4.1}$$

Insertion of $Z(\beta)$ if known, plus the given $V(x)$, evidently relates $A(\beta)$ and $K(\beta)$.

A. Use of a generalized "idempotency" condition

For the generalized off-diagonal density $\rho(x,x')=\sum_{\varepsilon_i<\mu}\psi_i(x)\psi_i^*(x')$ one knows that the orthonormality of the one-electron wave functions implies that it is an idempotent matrix, i.e. $\rho^2=\rho$. In coordinate representation this can be written quite explicitly as

$$\rho(x,x')=\int_{-\infty}^{\infty}dx''\rho(x,x'')\rho(x'',x') \ . \tag{4.2}$$

Using the orthogonality of the wave functions for the canonical or Bloch density matrix one can soon verify that [11]

$$Z(\beta+\beta')=\int_{-\infty}^{\infty}dx\int_{-\infty}^{\infty}dx'C(x,x',\beta)C(x',x,\beta') \ . \tag{4.3}$$

We now explore the limit when β' tends to zero. In this limit one can perform the Taylor expansion

$$Z(\beta+\beta')=Z(\beta)+Z'(\beta)\beta'+0(\beta')^2 \ , \tag{4.4}$$

$$\begin{aligned} Z(\beta+\beta')&=\frac{2A(\beta)}{(2\pi\beta')^{1/2}}\int_{-\infty}^{\infty}d\eta\,\exp\left[-\frac{2\eta^2}{K(\beta)}-\frac{2\eta^2}{\beta'}\right]\int_{-\infty}^{\infty}d\xi\,\exp[-\beta'V(\xi)-K(\beta)V(\xi)] \\ &=\frac{2A(\beta)}{(2\pi\beta')^{1/2}}\int_{-\infty}^{\infty}d\eta\left[1-\frac{2\eta^2}{K(\beta)}+\cdots\right]\exp\left[\frac{-2\eta^2}{\beta'}\right]\int_{-\infty}^{\infty}d\xi[1-\beta'V(\xi)+\cdots]\exp[-K(\beta)V(\xi)] \ . \end{aligned} \tag{4.5}$$

This leads to the result

$$Z'(\beta)=-\frac{Z(\beta)}{2K(\beta)}+A(\beta)\frac{\partial}{\partial K(\beta)}\left[\frac{Z(\beta)}{A(\beta)}\right]. \tag{4.6}$$

B. Harmonic-oscillator example

To show the way the above procedure works out, let us return briefly to the harmonic-oscillator example. The partition function $Z(\beta)$ has the form

$$Z(\beta)=\frac{\exp(-\beta\omega/2)}{1-\exp(-\beta\omega)} \tag{4.7}$$

yielding

$$Z'(\beta)=-\frac{\omega Z(\beta)}{2\tanh(\beta\omega/2)}. \tag{4.8}$$

One has also from Eq. (4.1) with $V(x)=\frac{1}{2}\omega^2x^2$,

$$Z(\beta)=A(\beta)\left[\frac{2\pi}{K(\beta)\omega^2}\right]^{1/2}. \tag{4.9}$$

Using Eqs. (4.9) in (4.6) yields

$$-\frac{Z'(\beta)}{Z(\beta)}=\frac{1}{2K(\beta)}-\frac{\partial}{\partial K(\beta)}\left[\frac{1}{2}\ln\left[\frac{2\pi}{K(\beta)\omega^2}\right]\right]=\frac{1}{K(\beta)}. \tag{4.10}$$

Hence it follows that

$$K(\beta)=\frac{2}{\omega}\tanh\left[\frac{\beta\omega}{2}\right] \tag{4.11}$$

and using this result with Eqs. (4.7)–(4.9) one finds

$$A(\beta)=\left[\frac{\omega}{2\pi\sinh(\beta\omega)}\right]^{1/2}. \tag{4.12}$$

Thus in this admittedly favorable case for the present approach, Eqs. (4.1) and (4.6) relating $A(\beta)$ and $K(\beta)$ via $V(x)$ and the partition function $Z(\beta)$ lead back to the exact results. What we propose is that these two equations provide a useful way of evaluating the temperature-dependent functions in the approximate Slater sum (2.6) for any one-dimensional potential $V(x)$ for which the integral (4.1) exists. The appendix considers a little further the off-diagonal canonical density matrix in terms of the effective potential matrix introduced earlier by Hilton, March, and Curtis [2].

V. SUMMARY

The main result of the paper for the off-diagonal form of the Slater sum is Eq. (2.6) for one dimension. This result is exact when third and higher derivatives of $V(x)$ are zero; otherwise it may well provide a useful approximation for other potentials with judicious choice of $A(\beta)$ and $K(\beta)$. A further point to be emphasized in the separation in sum and difference coordinates ξ and η is that $K(\beta)$ enters the two spatially dependent factors in a reciprocal manner.

As to the forms of $A(\beta)$ and $K(\beta)$, it may well be that there will be problems in which the partition function $Z(\beta)$ can be calculated, when the Slater sum cannot. Then $Z(\beta)$ can be used directly to relate $A(\beta)$ and $K(\beta)$ via the potential $V(x)$ through Eq. (4.1). To complete the determination of the temperature dependence of the Slater sum, we have utilized the "generalized idempotency" condition (4.3). The resulting equation relating $A(\beta)$ and $K(\beta)$ is exact for the harmonic potential.

In the appendix, via the potential matrix U, it is shown that a previously neglected nonlinear term $\beta^2|\nabla U|^2$ appearing in an integral equation for U can be approximated inside the integral when $K(\beta)$ is known. This term can then be readily incorporated, in transcending the existing linear response theory for U

Finally, it is tempting to speculate that it may be useful even in three dimensions to attempt to approximate $C(\mathbf{r},\mathbf{r}_0,\beta)$ by a form analogous to Eq. (2.6) with $\xi\rightarrow\frac{1}{2}(\mathbf{r}+\mathbf{r}_0)$ and $\eta\rightarrow\frac{1}{2}(\mathbf{r}-\mathbf{r}_0)$. Again knowledge of the partition function, plus generalized idempotency, would lead then to relations between $A(\beta)$ and $K(\beta)$. The incorporation of the nonlinear term in the three-dimensional generalization of Eq. (A2) for the effective potential matrix will again be feasible, as a direct generalization of the one-dimensional procedure discussed in the appendix. But, unfortunately the separable solution of the three-dimensional equation of motion for $C(\mathbf{r},\mathbf{r}_0,\beta)$ does not follow through, and this must indicate that separability in vector sum and difference quantities is not the controlled approximation in three dimensions that it is in the one-dimensional case treated fully in the present study. Nevertheless, for modeling plasmas subjected to intense laser irradiation, the three-dimensional rule outlined above may offer a way forward, through employing numerical iterative procedures to calculate the effective potential matrix U via the three-dimensional generalization of Eq. (A2).

APPENDIX

Canonical density matrix and effective potential $U(x,x',\beta)$

The definition [2] of the effective potential is

$$C(x,x',\beta)=\frac{1}{(2\pi\beta)^{1/2}}\exp\left[-\frac{(x-x')^2}{2\beta}\right]\times\exp[-\beta U(x,x',\beta)]. \tag{A1}$$

The integral form of the Bloch equation yields [12] then for U

$$U(x,x',\beta)=\int_{-\infty}^{\infty}dx''\left[V(x'')-\frac{\beta^2}{2}\left[\frac{\partial U(x'',x',\beta)}{\partial x''}\right]^2\right]\times G_0(x,x',x'',\beta), \tag{A2}$$

where

$$G_0(x,x',x'',\beta)=\frac{1}{2\beta}\text{erfc}\left[\frac{|x''-x|+|x''-x'|}{(2\beta)^{1/2}}\right]\times(2\pi\beta)^{1/2}\exp\left[\frac{(x-x')^2}{2\beta}\right] \tag{A3}$$

with

$$\text{erfc}(x)=\frac{2}{\pi^{1/2}}\int_x^\infty e^{-u^2}du\,(x\geq 0)\ . \tag{A4}$$

Taking the logarithm of Eq. (A1) and comparing with the logarithm of Eq. (2.6), one readily finds

$$-\beta U(x,x',\beta)=\ln A(\beta)-K(\beta)V(\xi)-\ln C_0(\beta)-2\left[\frac{1}{K(\beta)}-\frac{1}{\beta}\right]\eta^2\ . \tag{A5}$$

Equation (A5) is useful, given an approximation for $K(\beta)$, to insert in the $\beta^2(\partial U/\partial x)^2$ term inside the integral in Eq. (A2). Normal linear-response theory puts this term at zero. It is to be noted from Eq. (A5) that only $K(\beta)$ is needed: not $A(\beta)$ for this approximate iterative approach. However, it seems clear that usually numerical methods will be needed to perform such iteration for a general potential $V(x)$.

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