CLOSED RELATION BETWEEN SINGLE-PARTICLE KINETIC ENERGY AND ELECTRON DENSITY IN ONE-DIMENSIONAL TWO-LEVEL SYSTEMS

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For a two-level problem in one dimension, an implicit relation is derived relating the kinetic energy density $t_s(x)$ to the electron density $\rho(x)$ plus its first and second derivatives. As an example, the harmonic oscillator potential is used to make this relation explicit.

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1. Introduction

It remains of considerable interest in density functional theory to derive the single-particle kinetic energy density $t_s(x)$ in terms of the electron density $\rho(x)$ and its low-order derivatives. One such approximate theory is Thomas–Fermi plus von Weizsäcker (TFW), which yields in one dimension the result

$$t_s^{\mathrm{TFW}}(x) = c_k \rho^3(x) + \frac{\hbar^2}{8m} \frac{\rho'(x)^2}{\rho(x)}. \tag{1.1}$$

Of course, Eq. (1.1) is true in this approximate theory in the sense that $t_s(x)$ is a functional of $\rho(x)$.

While the generalization of Eq. (1.1) to potentials and densities with arbitrarily fast variation in space remains important, our aim is more modest, namely to calculate $t_s(x)$ from the ground-state electron density $\rho(x)$ and its derivatives for the two-level problem. This leaves open the question of $t_s(x)$ as a functional of $\rho(x)$.

2. Two-level system described by density amplitude and phase

We refer to an earlier work [1] on the two-level problem which yields, with wave functions ψ_1 and ψ_2 and corresponding one-electron eigenvalues ε_1 and ε_2,

$$\sqrt{2}\psi_1 = \sqrt{\rho(x)}\cos\theta(x) \tag{2.1}$$

$$\sqrt{2}\psi_2 = \sqrt{\rho(x)}\sin\theta(x), \tag{2.2}$$

where the equation for the phase $\theta(x)$ is [2]

$$\theta'' + \frac{\rho'}{\rho}\theta' = 2\xi\sin(2\theta) \text{ with } \xi = (\varepsilon_1 - \varepsilon_2)/2. \tag{2.3}$$

The kinetic energy density t_s has the form

$$t_s = \frac{1}{8}\frac{(\rho')^2}{\rho} + \frac{1}{2}\rho(\theta')^2 - \frac{1}{4}\rho''. \tag{2.4}$$

Defining the quantity $Y(x)$ by

$$Y(x) = \frac{t_s}{\rho} - \frac{1}{8}\left(\frac{\rho'}{\rho}\right)^2 + \frac{1}{4}\frac{\rho''}{\rho}, \tag{2.5}$$

one has from Eq. (2.4)

$$(\theta')^2 = 2Y. \tag{2.6}$$

Hence

$$\theta(x) = \pm\sqrt{2}\int^x dz\sqrt{Y(z)}, \tag{2.7}$$

which is now to be employed in Eq. (2.3) to derive an implicit relation between $Y(x)$ and $\rho(x)$. After a little calculation, Eq. (2.3) then becomes

$$\pm Y'(x)[\sqrt{Y(x)}]^{-1} \pm 2\frac{\rho'}{\rho}\sqrt{Y(x)} = 2\sqrt{2}\xi\sin\left(\pm 2\sqrt{2}\int^x dz\sqrt{Y(z)}\right) \tag{2.8}$$

and the ambiguity of sign drops out since $\sin(-x) = -\sin(x)$. Solving this first-order differential equation for $Y'(x)$ then yields

$$\sqrt{Y(x)} = \rho(x)^{-1}$$

$$\times \exp\left\{\sqrt{2}\xi\int^x dz\left[[\sqrt{Y(z)}]^{-1}\sin\left(2\sqrt{2}\int^z du\sqrt{Y(u)}\right)\right]\right\}. \tag{2.9}$$

This equation is therefore the desired relation between $t_s(x)$ density and its first and second derivatives, as seen by invoking Eq. (2.5).

3. Example of linear harmonic oscillator

Using the results of Lawes and March [3] and March and Nalewajski [4] one readily finds for the first two levels occupied in a harmonic oscillator field

$$(\theta')^2 = \frac{2}{Z^2}, \qquad Z = 1 + 2x^2, \tag{3.1}$$

thus

$$Y = \frac{1}{2}(\theta')^2 = Z^{-2}. \tag{3.2}$$

But Z can be expressed in terms of ρ since for this example the density has the explicit form

$$\rho(x) = \pi^{-1/2}\exp(-x^2)Z = \pi^{-1/2}\exp\left(\frac{1-Z}{2}\right),\tag{3.3}$$

and $\theta(x)$ has the form [5]

$$\theta(x) = \arcsin\left(\frac{1}{\sqrt{1+x^2}}\right).\tag{3.4}$$

Hence

$$\ln\rho = \frac{1}{2} - \frac{1}{2}\ln\pi - \frac{1}{2}Z + \ln Z.\tag{3.5}$$

In terms of Y in Eq. (3.2), we then have

$$\ln\rho = \frac{1}{2} - \frac{1}{2}\ln\pi - \frac{1}{2}Y^{-1/2} + \frac{1}{2}\ln Y.\tag{3.6}$$

Finally, from Eq. (2.5) one can substitute for Y in terms of t_s, to relate t_s to ρ, ρ' and ρ''

$$t_s(x) = \frac{1}{8}\frac{(\rho')^2}{\rho} + \left(1 + 2x^2\right)^{-2}\rho - \frac{1}{4}\rho''.\tag{3.7}$$

4. Summary and conclusions

Equation (2.9), valid for two occupied levels in one dimension, is of some interest for density functional theory. However, since it has been derived by using, essentially, an Euler equation (i.e. Schrödinger's equation for the ψ_1 and ψ_2) it has not been proved to represent t_s as a functional of the electron density. It does, however, afford a route to calculate t_s from a given density, though it must be pointed out that the eigenvalue difference $\varepsilon_1 - \varepsilon_2$ also enters the equation. The results have been made quite explicit for the harmonic oscillator with two occupied levels. It is, in a sense, explained in the Appendix in which the use of Eq. (2.7) for the phase allows a formally exact generalization of the JWKB approximation to the wave functions ψ_1 and ψ_2.

As a final comment, let us return to Eq. (2.5). Multiplying by ρ and integrating over the whole space then yields the total kinetic single-particle energy as

$$T_s = \frac{1}{8}\int\frac{(\rho')^2}{\rho}\mathrm{d}x + \int\rho(x)Y(x)\mathrm{d}x.\tag{4.1}$$

From Eq. (2.9), as already emphasized, Y is determined completely by knowledge of $\rho(x)$ plus $(\varepsilon_1 - \varepsilon_2)/2$.

Appendix: Relation to JWKB theory

To relate the treatment above to JWKB theory [6, 7] let us return to the wave functions ψ_1 and ψ_2 in terms of the density amplitude $\sqrt{\rho(x)}$ and the phase $\theta(x)$ in Eq. (2.1) and (2.2). Using Eq. (2.7), we find for ψ_1 the result

$$\sqrt{2}\psi_1(x) = \sqrt{\rho(x)} \cos \left[\sqrt{2} \int^x dz \sqrt{Y(z)} \right]. \tag{A1}$$

But from Eq. (2.5), $Y(x)$ can be expressed in terms of the kinetic energy density $t_s(x)$ together with $\rho(x)$ and its derivatives. In the spirit of semiclassical theory, one can now:

a) Neglect the derivatives of the density.

b) Use the semiclassical form $c_k \rho^3(x)$ quoted in Eq. (1.1) for $t_s(x)$.

Hence

$$Y(x) \approx c_k \rho^2(x). \tag{A2}$$

But in the semiclassical limit the Euler equation for the density becomes

$$\mu = 3c_k \rho^2(x) + V(x), \tag{A3}$$

or

$$Y(x) \approx \frac{1}{3}[\mu - V(x)] \tag{A4}$$

and inserting this into Eq. (A1) leads to the oscillatory part of the wave function in the usual JWKB form. Presumably, the refined kinetic energy functional, inserted into Eq. (2.5) for $Y(x)$, would lead by substitution into Eq. (A1) to refined single-particle wave functions.

References

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