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Direct Derivation of the Schwinger Quantum Correction to the Thomas–Fermi Atom

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The Schwinger quantum correction to the classic Thomas–Fermi atom is directly derived by solving for the latter without recourse to a modeling after the harmonic oscillator potential and without solving for the particle density.

In an ingenious treatment of the quantum correction to the remarkable Thomas–Fermi atom (Thomas, 1927; Fermi, 1927, 1928), Schwinger (1981) modeled his analysis after the harmonic oscillator potential. Although this modeling argument turns out to be correct, the importance of this "atom," which has captivated physicists since its birth over 70 years ago when quantum mechanics was still in its infancy, and will continue to do so due to its extreme simplicity and remarkable success, has motivated us to supply a direct derivation of the Schwinger correction without recourse to a harmonic oscillator potential modeling and without solving for the particle density (Dreizler and Gross, 1990). The latter reference also gives a fairly recent review of the state of the art of the theory and gives extensive references to the monumental work of Schwinger and to many other contributors. For more recent work and additional references see Morgan (1996).

The quantum correction to the ground-state energy is given by the compact expression

$$\delta E_{\text{Qua}} = \int d^3\bar{r}\, \frac{2}{2\pi i} \int_{-\infty}^{\infty} \frac{d\tau}{\tau - i\varepsilon}\, i\, \frac{\partial}{\partial \tau} [\delta G_0\, (\bar{r}\tau, \bar{r}0;\, V_{\text{TF}}) - \delta G_0(\bar{r}\tau, \bar{r}0;\, V_c)] \tag{1}$$

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where the τ-integral projects out the negative spectrum; $G_0(\vec{r}\tau, \vec{r}\,'0; V)$ is defined in terms of the Green function: $G_\pm(\vec{r}t, \vec{r}\,'0) = \mp(i/\hbar)\Theta(\mp t)G_0(\vec{r}\tau, \vec{r}\,'0; V)$ with appropriate boundary conditions $G_\pm(\vec{r}t, \vec{r}\,'0) = 0$ for $t > 0$ and $t < 0$, respectively. Here $\tau = t/\hbar$. $G_\pm$ satisfies the differential equation

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

The potentials have the following familiar expressions:

$$V_{\mathrm{TF}}(\vec{r}) = -(Ze^2/r)f(x) \tag{3}$$

$$V_C(\vec{r}) = -(Ze^2/r)\,[1 + f'(0)(r/a)] \tag{4}$$

where $a = (3\pi/4)^{2/3}(\hbar/2me^2)Z^{-1/3}$, $x = r/a$, and $f(x)$ is the Thomas–Fermi function: $f(0) = 1$, and vanishes like x^{-3} for $x \to \infty$. In Eq. (1) the Coulombic contribution (4), describing the so-called tightly bound electrons near the nucleus, is appropriately subtracted out. δG_0 denotes the shift from the semi-classical limit.

Upon setting

$$G_0(\vec{r}\tau, \vec{r}\,'0; V) = \int \frac{d^3\vec{p}}{(2\pi\hbar)^3}\, e^{i\vec{p}\cdot(\vec{r}-\vec{r}\,')/\hbar} e^{-i[(p^2\tau/2m)+U]} \tag{5}$$

we have that U satisfies the differential equation ($U|_{\tau=0} = 0$):

$$-\frac{\partial}{\partial\tau}U + V(\vec{r}) - \frac{\hbar\vec{p}}{m}\cdot\vec{\nabla}U + \frac{\hbar^2}{2m}(\vec{\nabla}U)^2 + \frac{i\hbar^2}{2m}\vec{\nabla}^2U = 0 \tag{6}$$

The semiclassical limit is given by $U_0 = V(\vec{r})\tau$. It is easily checked from (6) that the leading shift δU in U from the semiclassical limit is given by

$$\delta U = -\frac{\hbar\tau^2}{2m}\vec{p}\cdot\vec{\nabla}V + \frac{\hbar^2\tau^3}{6m^2}(\vec{p}\cdot\vec{\nabla})^2V + \frac{\hbar^2\tau^3}{6m}(\vec{\nabla}V)^2 + \frac{i\hbar^2\tau^2}{4m}\vec{\nabla}^2V \tag{7}$$

Upon replacing $U = U_0 + \delta U$ in (5) and carrying out an elementary Gaussian integral, we obtain for δG_0

$$\begin{aligned}\delta G_0(\vec{r}\tau, \vec{r}0; V) &= \frac{\hbar^2\tau^2}{12m}\left(\frac{m}{2\pi i\tau}\right)^{3/2} e^{-iV(\vec{r})\tau}[\vec{\nabla}^2V - \frac{i\tau}{2}(\vec{\nabla}V)^2] \\ &= \frac{\hbar^2\tau^2}{12m}\int\frac{d^3\vec{p}}{(2\pi\hbar)^3}\, e^{-i[(p^2\tau/2m)+V(\vec{r})\tau]}\left[\vec{\nabla}^2V - \frac{i\tau}{2}(\vec{\nabla}V)^2\right]\end{aligned} \tag{8}$$

Upon integrating over τ in (1) by parts, we obtain for

$$\frac{2}{2\pi i}\int_{\infty}^{\infty}\frac{d\tau}{\tau - i\epsilon}\frac{i\partial}{\partial\tau}\,\delta G_0(\vec{r}\tau, \vec{r}0;\, V)$$

the remarkably simple expression

$$\frac{\hbar^2}{6m}\left[\vec{\nabla}^2 V + \frac{(\vec{\nabla}V)^2}{2}\frac{d}{dV}\right]\int\frac{d^3\vec{p}}{(2\pi\hbar)^3}\,\delta\!\left(\frac{p^2}{2m} + V(\vec{r})\right) \tag{9}$$

involving only *one* (!) derivative with respect to V. The latter expression is readily integrated to yield, after straightforward rearrangements of terms,

$$\frac{1}{24\pi^2\hbar}\left[(\vec{\nabla}^2 V)(-2mV)^{1/2} - \frac{1}{3m}\vec{\nabla}\cdot(\vec{\nabla}(-2mV)^{3/2})\right] \tag{10}$$

The second expression in (10) gives a zero surface contribution to (1) at infinity and near the origin due to the properties of

$$[(-2mV_{\mathrm{TF}}(\vec{r}))^{3/2} - (-2mV_{\mathrm{C}}(\vec{r}))^{3/2}] \text{ for } r \to \infty \text{ and } r \to 0.$$

Finally we use the following important relations for the potentials:

$$[(-2mV_{\mathrm{TF}}(\vec{r}))^{1/2} - (-2mV_{\mathrm{C}}(\vec{r}))^{1/2}]\delta^3(\vec{r}) = 0 \tag{11}$$

$$\vec{\nabla}^2 V_{\mathrm{TF}}(\vec{r}) = 4\pi Ze^2\delta^3(\vec{r}) - \frac{4}{3\pi}\left(\frac{2mZe^2}{r\hbar^2}\right)^{3/2}(f(x))^{3/2} \tag{12}$$

$$\vec{\nabla}^2 V_{\mathrm{C}}(\vec{r}) = 4\pi Ze^2\delta^3(\vec{r}) \tag{13}$$

and the first expression in (10) to immediately obtain for δE_{Qua} in (1)

$$\delta E_{\mathrm{Qua}} = -\frac{4}{9\pi^2}\left(\frac{3\pi}{4}\right)^{2/3}\left(\frac{me^4}{\hbar^2}\right)Z^{5/3}\int_0^{\infty} dx(f(x))^2 \tag{14}$$

accounting for the $-0.04907Z^{5/3}$ (in units of $me^4/\hbar^2$) contribution to the ground-state energy.

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