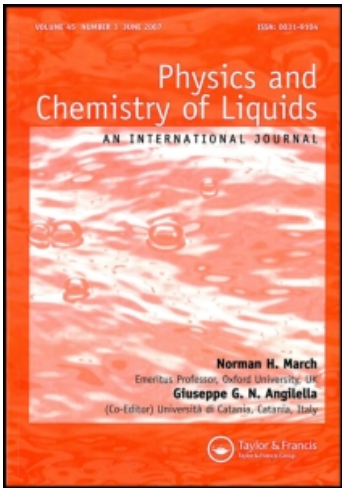

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X-ray scattering factor of the inhomogeneous electron liquid in the ground state of the Ne atom: contribution of the exchange-correlation potential

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LETTER

X-ray scattering factor of the inhomogeneous electron liquid in the ground state of the Ne atom: contribution of the exchange-correlation potential

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We have recently set out an approach to the X-ray scattering from 10-electron central field systems such as the almost spherical molecular species CH_4 and NH_4^+, in terms of DFT. Here, we take the united atom Ne of CH_4 as our focal point, and exploit the fact that the exchange-correlation potential $V_{xc}(r)$ is known from the work of Zhao *et al.* (Q. Zhao, R.C. Morrison and R.G. Parr, Phys. Rev. **A50**, 2138 (1994)). Thus, we can calculate the explicit and sizeable contribution that the exchange-correlation force $-\partial V_{xc}/\partial r$ derived from this exchange-correlation potential makes to the measured X-ray scattering factor of Ne.

Keywords: inhomogeneous electron liquid; Ne atom; X-ray scattering; exchange-correlation potential

In 10-electron central field problems with spherical ground-state electron density $\rho(r)$, we have recently re-written [1] the X-ray scattering factor $f(k)$, defined as the Fourier transform of $\rho(r)$, namely

$$f(k) = \int_0^\infty \rho(r) 4\pi r^2 \frac{\sin kr}{kr} \mathrm{d}r, \tag{1}$$

in terms of the total number of electrons $Q(r)$ within a sphere of radius r centred on the central nucleus; in the example below that for the Ne atom. Since $Q(r)$ is by definition related to $\rho(r)$ in Equation (1) by

$$Q(r) = \int_0^r \rho(r) 4\pi r^2 \mathrm{d}r, \tag{2}$$

we have

$$\frac{\partial Q(r)}{\partial r} = \rho(r) 4\pi r^2. \tag{3}$$

Inserting Equation (3) into Equation (1) and after integration by parts we obtain the result

$$f(k) = k \int_0^\infty Q(r) j_1(kr) \mathrm{d}r, \tag{4}$$

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where $j_1(x) = (\sin x - x\cos x)/x^2$ is the first-order spherical Bessel function. But using an earlier result by one of us [2], the one-body potential of DFT enters the force equation

$$-\frac{\partial V(r)}{\partial r} = -\frac{\partial V_{\text{ext}}}{\partial r} + \frac{Q(r)e^2}{r^2} - \frac{\partial V_{xc}}{\partial r}. \tag{5}$$

We can therefore substitute for $Q(r)$ in Equation (4) to obtain the DFT form of the X-ray scattering factor $f(k)$ as

$$f(k) = k\int_0^\infty -r^2\frac{\partial}{\partial r}(V(r) - V_{xc}(r))j_1(kr)\mathrm{d}r + f_{\text{ext}}(k), \tag{6}$$

where $f_{\text{ext}}(k)$ is given in terms of the known external potential V_{ext} appearing in Equation (5) by

$$f_{\text{ext}}(k) = k\int_0^\infty r^2\frac{\partial V_{\text{ext}}}{\partial r}j_1(kr)\mathrm{d}r. \tag{7}$$

But for the Ne atom, which is our focus here,

$$V_{\text{ext}}(r) = -\frac{10e^2}{r} \tag{8}$$

and hence

$$\frac{\partial V_{\text{ext}}(r)}{\partial r} = \frac{10e^2}{r^2}. \tag{9}$$

Substituting Equation (9) in Equation (7) yields

$$f_{\text{ext}}(k) = 10. \tag{10}$$

Hence, using the known scattering factor of Ne [3], we plot $f(k) - f_{\text{ext}}(k)$ as curve 1 in Figure 1. Our aim below is now to exhibit the contribution which the force $-\partial V_{xc}/\partial r$ derived from the exchange-correlation potential $V_{xc}(k)$ makes to Figure 1. Therefore, we next define

$$f_{xc}(k) = k\int_0^\infty r^2\frac{\partial V_{xc}}{\partial r}j_1(kr)\mathrm{d}r. \tag{11}$$

As the large r form of $V_{xc}(r)$ is known to decay as $-e^2/r$, it is convenient to split the integral appearing in Equation (11) into two parts:

$$\begin{aligned} k\int_0^\infty r^2\frac{\partial V_{xc}}{\partial r}j_1(kr)\mathrm{d}r &= k\int_0^R r^2\frac{\partial V_{xc}}{\partial r}j_1(kr)\mathrm{d}r + k\int_R^\infty r^2\frac{\partial V_{xc}}{\partial r}j_1(kr)\mathrm{d}r \\ &= f_1(k,R) + f_2(k,R). \end{aligned} \tag{12}$$

The two integrals, f_1 and f_2, defined in Equation (12) must, of course, sum to give a result independent of the choice of R. Taking R sufficiently large to replace $\partial V_{xc}/\partial r$ by its asymptotic large r from e^2/r^2, we readily find, in atomic units ($e = 1$),

$$f_2(k,R)|_{R\to\infty} = k\int_R^\infty j_1(kr)\mathrm{d}r. \tag{13}$$

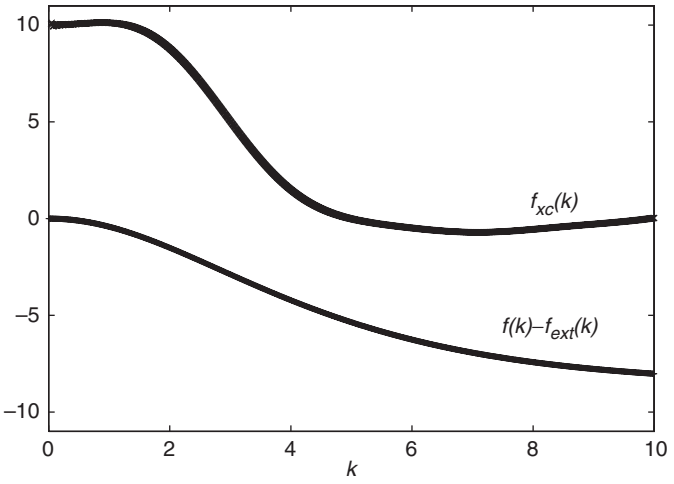

Figure 1. X-ray scattering factor contribution $f(k)-f_{\text{ext}}(k)$ ($f(k)$ taken from [3]) and $f_{xc}(k)$ defined in Equation (11), for which the force $-\partial V_{xc}/\partial r$ is taken from Figure 3.

But $j_1(x) = -(\partial/\partial x)\ (\sin x/x)$, and hence

$$f_2(k, R)|_{R\to\infty} = \frac{\sin kR}{kR}. \tag{14}$$

Below, we shall therefore study $f_1(r, R)$ defined in Equation (12) numerically for two large values of R. To do so, we utilise the work of Zhao, *et al.* [4] who were concerned with calculating $V_{xc}(r)$ for the Ne atom. We reproduce their plot of this quantity in Figure 2, where it can be seen that there is a turning point (maximum) at $r = 0.33$ au and a gentle minimum at a slightly larger value of $r = 0.43$ au. We have added a further curve to Figure 2 to show the large r asymptote to $-1/r$ in au. This is already a useful approximation beyond $r = 2$, and we have therefore taken two values of R in Equation (12), namely $R = 3$ and 5 au. Returning to Figure 1, we have then plotted the sum on the RHS of Equation (12) for these choices of R, using Equation (14) for $f_2(k, R)$ in each case.

For the future, it will be of interest to study whether a small change in the derivative $\partial V_{xc}/\partial r$ plotted in Figure 3 can markedly affect the plot of $f_{xc}(k)$ in Figure 1. Therefore, we draw attention to the large r result [2,5]

$$V_{xc}(r) = -\frac{1}{r} - \frac{\alpha}{2r^4} + \cdots, \tag{15}$$

where α is the static polarisability of Ne to fit on to the Zhao *et al.* [4] data reproduced in Figure 2.

As a final objective of the present study, we have attempted to fit the exchange-correlation potential $V_{xc}(r)$. We chose to employ the fit form

$$V_{xc}(r) = -\frac{1}{r+a} - \frac{\alpha}{2(r + b\sqrt{r} + c)^4}, \tag{16}$$

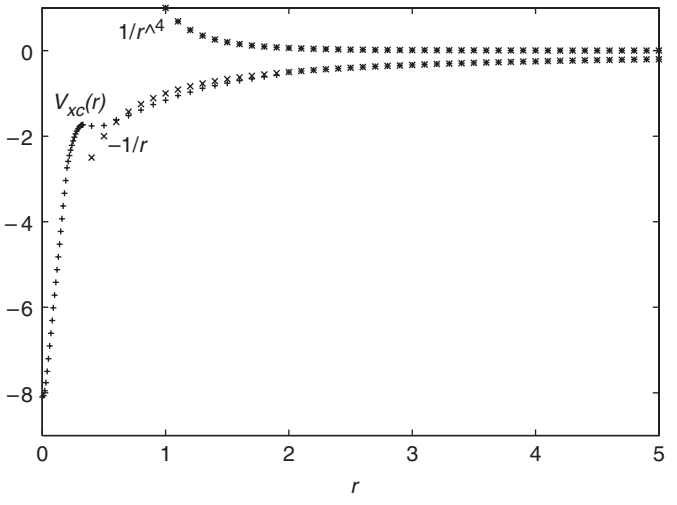

Figure 2. Shows exchange-correlation potential $V_{xc}(r)$ (+symbols) taken from [4], together with leading term $-1/r$ (×symbols) which is asymptotically correct as r tends to infinity. The next term in Equation (15) at large r is also plotted in the form $1/r^4$ (∗symbols). Units are au both for r and $V_{xc}(r)$.

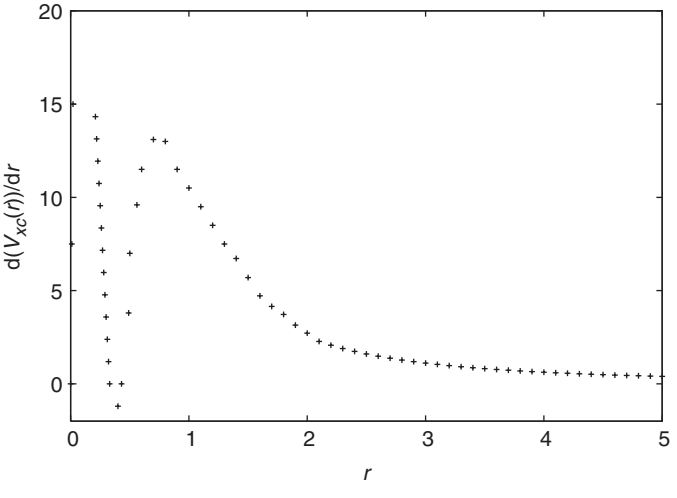

Figure 3. Shows the derivative of the exchange-correlation potential $V_{xc}(r)$ for neon, the latter being taken from [4]. Units are au both for r and $V_{xc}(r)$.

where a, b and c are fitting parameters. The first choice of these was: $a = 0.127$, $b = -1.589$, $c = 1.336$ (fit 1, displayed in Figure 4). In this case, the three equations used to fit the curve were

$$\begin{aligned} V_{xc}(0) &= -8.1 \\ \frac{\mathrm{d}V_{xc}(0.33)}{\mathrm{d}r} &= 0 \text{ (maximum)} \end{aligned} \tag{17}$$

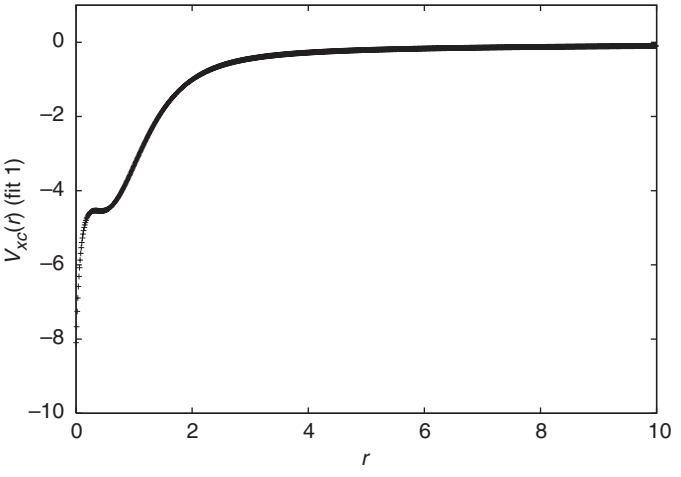

Figure 4. Parametrised form of $V_{xc}(r)$ according to Equation (16), with parameters a, b and c being the parameters for fit 1. Units are au both for r and $V_{xc}(r)$.

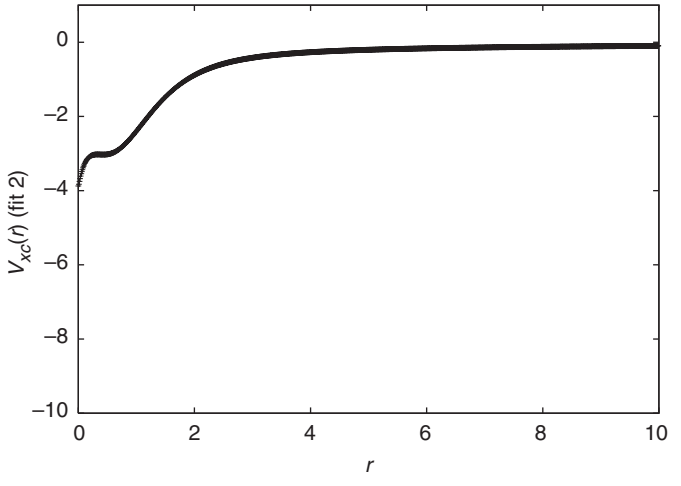

Figure 5. Same as Figure 4, but with the parameters a, b, c for fit 2. Units are au both for r and $V_{xc}(r)$.

$$\frac{\mathrm{d}V_{xc}(0.43)}{\mathrm{d}r} = 0 \text{ (minimum).}$$

After a number of trial runs, a slightly improved curve (fit 2, displayed in Figure 5) was fitted using the parameters : $a = 0.269$, $b = -1.660$, $c = 1.488$, where a of course is substantially different from the value adopted to yield curve 1. The equations analogous in Equation (17) were then

$$V_{xc}(0.20) = -2.74$$

$$\frac{dV_{xc}(0.33)}{dr} = 0 \text{ (maximum)}$$
$$\frac{dV_{xc}(0.43)}{dr} = 0 \text{ (minimum).} \tag{18}$$

Of course, for Ne we already have an excellent form of $V_{xc}(r)$ given by Parr and co-workers, with which our semiempirical forms can be compared.

In summary, starting from the X-ray scattering factor $f(k)$ for Ne given in [3], we show how the Zhao *et al*. form of the force $-\partial V_{xc}/\partial r$ contributes to this experimentally accessible quantity $f(k)$ for the Ne atom. We emphasise that it is fundamentally the force $-\partial V_{xc}/\partial r$ rather than the potential $V_{xc}(r)$ which determines the contribution of the exchange plus correlation to the X-ray scattering. Of course, refined X-ray experiments on Ne would be valuable in tightening up the numerical accuracy of the present analysis. Naturally, existing functionals (of which there are many: see, for example, [6]) could be tested using the present analysis of X-ray measurements, but it is not our purpose to pursue that aspect here.

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