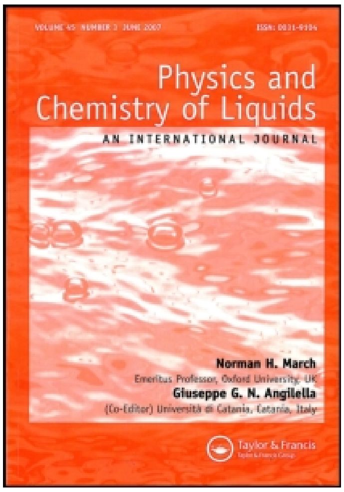

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Proposal for extraction of the exchange correlation potential of DFT from X-ray scattering measurements on the 'almost spherical' inhomogeneous electron liquids in CH_4 and NH_4^+

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Experimental X-ray scattering data exists on the inhomogeneous electron liquids in the almost spherical 10-electron systems CH_4 and NH_4^+. Furthermore, simple but realistic models are available which accurately represent the X-ray data. These are here utilised to construct a route to estimate the force $-\partial V(r)/\partial r$ where $V(r)$ is the one-body potential of DFT. The total number of electrons, $Q(r)$ say, inside a sphere of radius r around the central atom, C or N, is the essential input from the X-ray data. Quantum chemical calculations can then be used to divide the total ground-state density into s and p contributions. Using the general theory available for 10-electron central field systems, a proposal for extracting the exchange correlation force $-\partial V_{xc}/\partial r$ from X-ray data for both CH_4 and NH_4^+ is put forward, V_{xc} being the exchange correlation potential of DFT.

Keywords: Inhomogeneous electron liquids; 10-Electron molecules; X-ray scattering factor

1. Introduction

In recent work [1], we used Hartree–Fock (HF) theory for the ground state of the 10-electron molecules CH_4, NH_3 and H_2O to extract the exchange energy density $\epsilon_x(\vec{r})$. This was defined from the Dirac expression [2] for the total exchange energy E_x, namely,

$$E_x = -\frac{e^2}{4}\int \frac{\gamma^2(\vec{r},\vec{r'})}{|\vec{r}-\vec{r'}|}\,d\vec{r}\,d\vec{r'} \tag{1}$$

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where $\gamma(\vec{r},\vec{r'})$ is the first-order density matrix built from the doubly occupied HF orbitals $\psi_i(\vec{r})$ as

$$\gamma(\vec{r},\vec{r'}) = 2\sum_{\text{occ } i} \psi_i^*(\vec{r})\psi_i(\vec{r'}) \tag{2}$$

Of course, γ has the HF ground-state electron density $\rho(\vec{r})$ on its diagonal: i.e.

$$\gamma(\vec{r},\vec{r'})\,|_{\vec{r'}=\vec{r}} = \rho(\vec{r}) \tag{3}$$

From (1) and (2), the exchange energy density $\epsilon_{\text{x}}(\vec{r})$ was defined as

$$\epsilon_{\text{x}}(\vec{r}) = -\frac{e^2}{4}\int \frac{\gamma^2(\vec{r},\vec{r'})}{|\vec{r}-\vec{r'}|}\,\mathrm{d}\vec{r'} \tag{4}$$

and evidently from equations (1) and (4), we have

$$E_{\text{x}} = \int \epsilon_{\text{x}}(\vec{r})\,\mathrm{d}\vec{r} \tag{5}$$

Unfortunately, to date, it has not proved possible to find the exchange potential $V_{\text{x}}(\vec{r})$ defined by [3]

$$V_{\text{x}}(\vec{r}) = \frac{\delta E_{\text{x}}[\rho]}{\delta\rho(\vec{r})} \tag{6}$$

since the so-called Dirac density matrix γ in equation (2) is not known as a functional of its diagonal density ρ, though some progress along this route has been reported recently [4].

Because of the continuing interest in the exchange correlation potential $\mathrm{V}_{\text{xc}}(\vec{r})$, we have considered again the united atom, Ne, of the three 10-electron molecules cited earlier treated previously from a quantum Monte Carlo (QMC) density as a starting point [5]. It has been recognised since the early work of March and Santamaria [6] on the large Z non-relativistic limit of the 10-electron Ne-like atomic ions that $\gamma(\vec{r},\vec{r'})$ has especially simple properties for the case of K plus L closed shells. This simplication for the general 10-electron central field problem was set out by Howard *et al.* [7]. These authors wrote the density matrix $\gamma(\vec{r},\vec{r'})$ for this case as

$$\gamma(\vec{r},\vec{r'}) = \Gamma(\vec{r},\vec{r'}) \;-\; 3\,f(r)f(r')\,|\,\vec{r}-\vec{r'}\,|^2 \tag{7}$$

where evidently, by means of equation (3), $\Gamma(r,r) = \rho(r)$. If the ground state density $\rho(r)$ for Ne is written as

$$\rho(r) = \rho_{\text{s}}(r) + \rho_{\text{p}}(r) \tag{8}$$

where $\rho_s(r)$ is the contribution from the 1s and 2s electrons, while $\rho_p(r)$ is the density of the p shell, then in [7] it was demonstrated that $f(r)$ in equation (7) was related to $\rho_p(r)$ by

$$\rho_p(r) = 6r^2 f^2(r) \tag{9}$$

More recently, one of us [8] has followed up the work of March and Suhai [4] on the density matrix $\gamma(\vec{r}, \vec{r}')$ for one- and two-level occupancy by seeking a form $\gamma[\rho, t_g]$ for the Dirac matrix defined in equation (2) with three levels filled, where t_g is the positive definite kinetic energy density defined from the wave function form $(\nabla\psi)^2$. Again, it is useful to divide t_g into s and p contributions which, in the spherically symmetric Ne atom plus the almost spherical systems CH_4 and NH_4^+, will be written as $t_s(r)$ and $t_p(r)$. Then using results of [7] and early articles cited there, it was shown in [8] that

$$t_p(r) = \frac{\rho_p(r)}{r^2} + \frac{1}{8}\frac{\rho_p'^2(r)}{\rho_p(r)}. \tag{10}$$

One of us [9] has earlier advocated an 'electrostatic' approach to the exchange correlation potential $V_{xc}(r)$ [3] of Density Functional Theory (DFT). Thus, in [9], one has, with $V(r)$ denoting the one-body potential energy of DFT [3] in spherical systems (Ne and the 'almost spherical' CH_4 and NH_4^+ to be discussed more in detail further), the force equation [9]:

$$-\frac{\partial V(r)}{\partial r} = -\frac{\partial V_{ext}}{\partial r} + \frac{Q(r)e^2}{r^2} - \frac{\partial V_{xc}(r)}{\partial r} \tag{11}$$

where $Q(r)$ is the total number of electrons inside a sphere of radius r, centred on the heavy atom, i.e. Ne, C or N. We set out immediately subsequently the form of the external potential term $-\partial V_{ext}/\partial r$ for Ne, CH_4 and NH_4^+ in turn. Thus we have:

(i) Ne atom,

$$-\frac{\partial V_{ext}}{\partial r} = -\frac{10e^2}{r^2} \tag{12}$$

(ii) CH_4 (cf. the earlier work of one of us [10], where the semiclassical Thomas–Fermi method, the forerunner of DFT, was however employed. Further, no semiclassical approximations are invoked for Ne, CH_4 or NH_4^+)

$$-\frac{\partial V_{ext}}{\partial r} = -\frac{6e^2}{r^2}, \quad r < R_e \tag{13}$$

$$= -\frac{10e^2}{r^2}, \quad r > R_e \tag{14}$$

where R_e denotes the equilibrium CH bond length.

(iii) NH_4^+:

$$-\frac{\partial V_{\text{ext}}}{\partial r} = -\frac{7e^2}{r^2}, \quad r < R_e \tag{15}$$

$$= -\frac{11e^2}{r^2}, \quad r > R_e \tag{16}$$

with R_e now the NH_4^+ equilibrium NH bond length.

With the above as background, a brief outline of the present article follows. In section 2, we address the form of $Q(r)$ introduced in equation (11). In [5], for the Ne atom this was calculated and displayed in figure 1 of that reference. For CH_4 and NH_4^+, $Q(r)$ is, instead, derived from measured X-ray scattering data, obtained by Thomer [11] and by McDonald [12] respectively.

2. Modelling $Q(r)$, the total number of electrons contained within a sphere of radius r centred on the central nucleus, from X-ray scattering experiments

For Ne we have redrawn in figure 1 the quantity $Q(r)$ defined precisely by

$$Q(r) = \int_0^r \rho(r) 4\pi r^2 \mathrm{d}r \tag{17}$$

where $\rho(r)$ is the ground-state QMC electron density for the Ne atom. The HF $Q(r)$ is also shown following [5], and differences from the QMC result are barely discernable graphically.

Our aim below is to use the X-ray measurements of Thomer [11] on CH_4 and of McDonald [12] on NH_4^+ to construct $Q(r)$ for these two 10-electron 'almost spherical' molecules.

Beginning with NH_4^+, McDonald himself produced an appealing "crystallographer's" model of the ground-state density $\rho(r)$ to fit his X-ray diffraction measurements. Thus, he considered a 2p electron of the central N 'atom' in NH_4^+ to be removed, leaving 6 electrons on the nitrogen nucleus. He then observed that to treat the remaining four 'p-like' electrons, he could allow unperturbed H atom densities to 'float inwards' from the 4 protons, to complete the $(1s)^2(2s)^2(2p)^6$ configuration when adapted to our central field model.

For NH_4^+, we take as starting point a 'spherically' averaged HF N atom from which one 2p electron has been removed. Then, with 6 'core electrons', we use McDonald's model of 'floating H densities' for the remaining 4 electrons, the H densities being centred at a distance r_0 along the NH bonds from the central N atom (figure 2).

Following Banyard and March [13] on NH_4^+, we write the radial density $D(r)$ of the remaining 4 electrons as

$$\begin{aligned} D_{4\mathrm{H}}(r, r_0) &= 4\pi r^2 \rho_{4\mathrm{H}}(r, r_0) \\ &= \left(\frac{2r}{r_0}\right)[\exp(-2\mid r - r_0 \mid)\{1 + 2\mid r - r_0 \mid\} - \exp(-2(r + r_0))\{1 + 2(r + r_0)\}] \end{aligned} \tag{18}$$

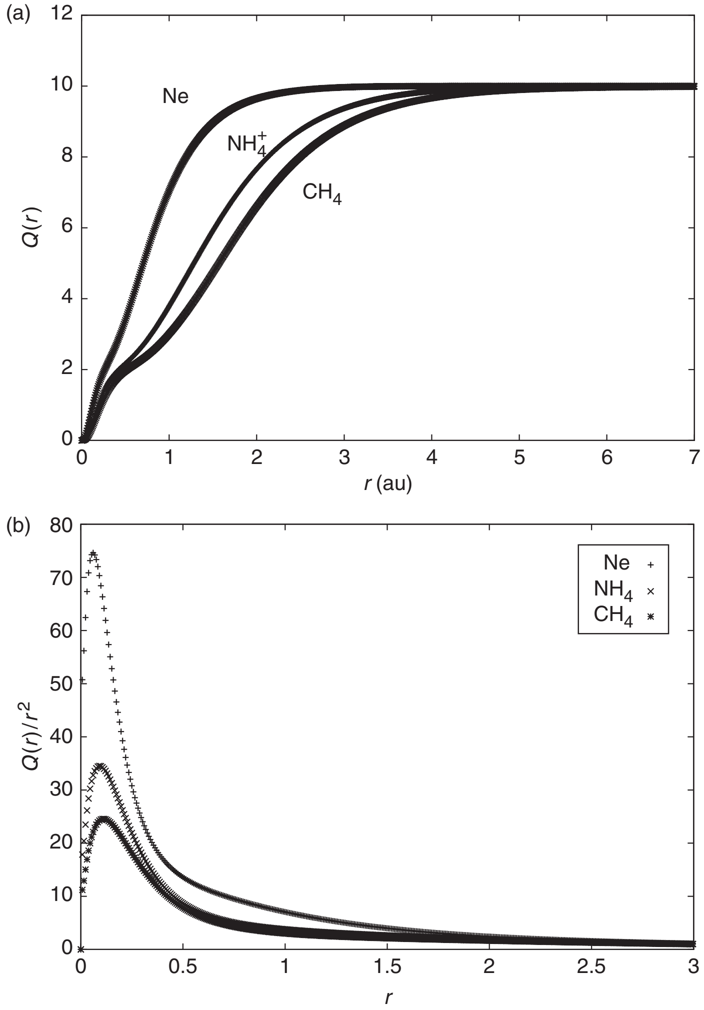

Figure 1. (a) Total number of electrons $Q(r)$ inside a sphere of radius r for the Ne atom both from the H–F method and from QMC, and from X-ray data for both CH_4 and NH_4^+. (b) $Q(r)$ from figure 1(a) divided by r^2, as in equation (11).

where

$$\int_0^\infty D_{4\mathrm{H}}(r)\mathrm{d}r = 4 \tag{19}$$

and hence the spherically averaged scattering factor is given by

$$\begin{aligned} f_{4\mathrm{H}}(r, r_0) = &\int_0^{r_0} \left(\frac{2r}{r_0}\right)[\exp(-2(r_0 - r))\{1 + 2(r_0 - r)\} - \exp(-2(r + r_0))\{1 + 2(r + r_0)\}] \\ &+ \int_{r_0}^\infty \left(\frac{2r}{r_0}\right)[\exp(-2(r - r_0))\{1 + 2(r - r_0)\} - \exp(-2(r + r_0))\{1 + 2(r + r_0)\}]. \end{aligned} \tag{20}$$

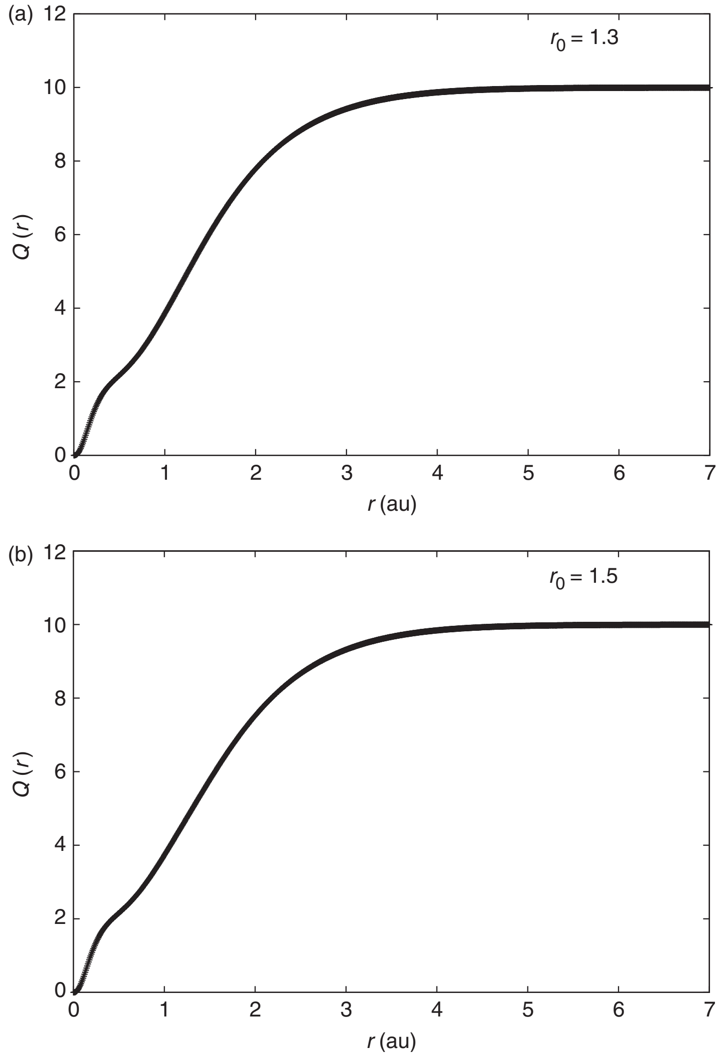

Figure 2. $Q(r)$ for NH_4^+ for different distances r_0 from the N atom for floating H atom densities in the model of McDonald: (a) $r_0 = 1.3$ au, (b) $r_0 = 1.5$ au.

Then, we must add

$$f_N^{\text{less one 2p elec.}}(k) = \int_0^\infty \rho_N^+(r) 4\pi r^2 \frac{\sin(kr)}{kr} \mathrm{d}r \tag{21}$$

where

$$k = 4\pi \frac{\sin(\theta/2)}{\lambda} \tag{22}$$

with λ the X-ray wavelength and θ the scattering angle.

Earlier, Banyard and March [13] constructed from the McDonald model of $\rho(r)$, an 'average' spherical density $\rho(r)$. Using this approach, $Q(r)$ has then been calculated from equation (15), and is plotted for comparison with the results of [5] for the Ne atom in figure 1(a).

A similar approach for CH_4 has been employed to fit the X-ray measured data of Thomer [11], and $Q(r)$ thereby calculated is also displayed in figure 1(a).

3. Proposal to model force $-\partial V/\partial r$ in equation (11) from knowledge of p-state density

Having discussed in section 2 the first two terms on the RHS of equation (11), we turn to our proposal to estimate the LHS, namely the force $-\partial V/\partial r$ associated with the one-body potential $V(r)$. We appeal to a result given in [8], namely

$$-\frac{\partial V}{\partial r} = \frac{2}{r^2\rho_{\mathrm{p}}}\frac{\partial}{\partial r}[r^2\ t_{\mathrm{p}}] - \frac{1}{4}\frac{\rho_{\mathrm{p}}'''}{\rho_{\mathrm{p}}} - \frac{1}{2r}\frac{\rho_{\mathrm{p}}''}{\rho_{\mathrm{p}}} - \frac{3}{2}\frac{\rho_{\mathrm{p}}'}{r^2\rho_{\mathrm{p}}} - \frac{2}{r^3}. \tag{23}$$

But since we have already given the p-state kinetic energy $t_{\mathrm{p}}(r)$ appearing in the first term on the RHS of equation (21) in terms of the p-state density $\rho_{\mathrm{p}}(r)$ in equation (10), our proposal is to determine the force $-\partial V/\partial r$ solely from $\rho_{\mathrm{p}}(r)$.

In the previous section, we gave the explicit forms of $-\partial V_{\mathrm{ext}}/\partial r$ for CH_4 and NH_4^+. Thus the only term in equation (11) needed to calculate the derived exchange correlation force $-\partial V_{\mathrm{xc}}(r)/\partial r$ is the quantity $Q(r)e^2/r^2$. This is therefore plotted, in atomic units, *versus* r in figure 1(b). We intend, in a later article, to present numerical results for $-\partial V_{\mathrm{xc}}/\partial r$ of CH_4 and NH_4^+, using as input $Q(r)e^2/r^2$ as shown in figure 1(b). Therefore we are presently studying quantitatively the p-state density $\rho_{\mathrm{p}}(r)$ in these two, almost spherical, molecular systems, by quantum chemical methods. Also, we intend to examine the separate contributions made by the various terms in equation (11) to the measured scattering factors $f(k)$ for CH_4 and NH_4^+. Therefore, we have plotted these quantities in figure 3, where the result for the Ne atom is also shown for comparison.

4. Summary and future directions

For the almost spherical systems CH_4 and NH_4^+, the inhomogeneous electron liquid is characterised by the number of electrons within a sphere of radius r centred on the C or N nuclei, and denoted by $Q(r)$. Figure 1(a) shows what are the essential results for $Q(r)$ obtained from experimental X-ray scattering studies [11,12]. For comparison, the result for the Ne atom is also shown, $Q(r)$ being indistinguishable in this case from HF compared with QMC studies [5]. Figure 1(a) represents the essential input for the present proposal to extract $\partial V_{\mathrm{xc}}/\partial r$ from experiment. The second step is to determine $-\partial V/\partial r$ entering in equation (11) from p-state information, via eqnuations (8), (10) and (21). Then, given $Q(r)$ in equation (11), an estimate of $\partial V_{\mathrm{xc}}/\partial r$ will result.

As for future directions, we are studying how equation (11) can be put directly into the form of an equation for the scattering factor $f(k)$ defined for example

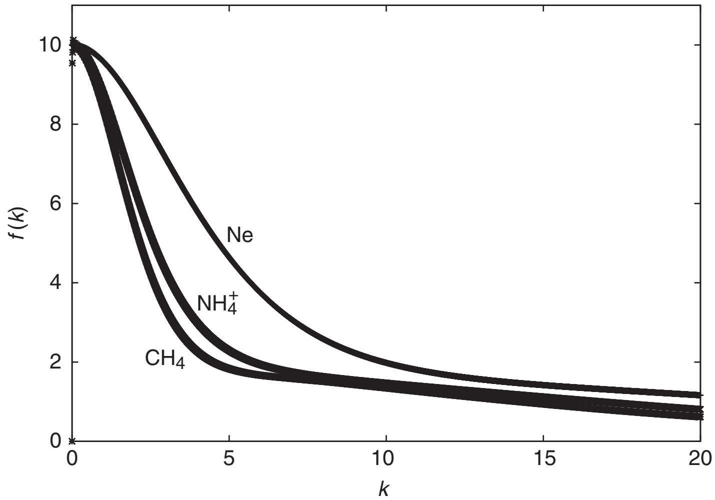

Figure 3. Measured X-ray scattering factors *f*(*k*) as reproducing theoretical modelling of X-ray diffraction measurements for CH_4 and NH_4^+. The result for *f*(*k*) for the Ne atom is also shown for comparison.

in equations (20, 21). This should permit us to assess what contribution the exchange correlation force $-\partial V_{xc}/\partial r$ appearing in equation (11) makes to the measured scattering factor *f*(*k*). We intend to report subsequently such results for CH_4 and NH_4^+ which represent the focus of the present article.

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References

[1] C. Van Alsenoy, N.H. March. *Phys. Chem. Liqu.* **45**, 15 (2007).
[2] P.A.M. Dirac. *Proc., Camb. Phil. Soc.*, **26**, 376 (1930).
[3] R.G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York (1989).
[4] N.H. March, S. Suhai. *Phys. Lett. A*, **360**, 665 (2007).
[5] I.A. Howard, K.D. Sen, P. Geerlings. N.H. March. *J. Phys. B: At. Mol. Phys.*, **38**, 1705 (2005).
[6] N.H. March, R. Santamaria. *Phys. Rev.*, **A38**, 5002 (1988).
[7] I.A. Howard, N.H. March, A. Nagy, V.E. Van Doren. *Phys. Chem. Liqu.*, **40**, 47 (2002).
[8] N.H. March. Int. Centre for Theor. Phys. Trieste, Internal Report (2007) (In press).
[9] N.H. March. *Phys. Rev.*, **A65**, 034501 (2002).
[10] N.H. March. *Proc. Camb. Phil. Soc.*, **48**, 665 (1952).

[11] G. Thomer. *Phys. Zeits.*, **38**, 48 (1937); see summary in Appendix A4: 10 of N.H. March, J.F. Mucci. *Chemical Physics of Free Molecules*, Plenum Press, New York (1993).
[12] T.R.R. McDonald. *Acta Cryst.*, **3**, 113 (1960); C. Carter. *Proc. Roy. Soc.*, **A235**, 321 (1956); I.M. Mills. *Mol. Phys.*, **4**, 57 (1961).
[13] K.E. Banyard. N.H. March. *Acta Cryst.*, **14**, 357 (1961).