10 SCIENTIFIC HIGHLIGHT OF THE MONTH

Spin fluctuations in nearly magnetic metals from ab-initio dynamical spin susceptibility calculations

J.B. Staunton[1], J. Poulter[2], B. Ginatempo[3], E. Bruno[3] and D.D. Johnson[4]

[1] *Department of Physics, University of Warwick,Coventry CV4 7AL, U.K.*

[2] *Department of Mathematics,Faculty of Science, Mahidol University,Bangkok 10400, Thailand.*

[3] *Dipartimento di Fisica and Unita INFM, Universita di Messina, Italy*

[4] *Department of Materials Science and Engineering, University of Illinois, IL 61801, U.S.A.*

There has been renewed interest in spin fluctuations in materials close to magnetic order recently. This is due in part to a realisation that nearly critical magnetic fluctuations may be important factors governing the non-conventional properties of a wide range of materials which include the high T_c superconducting cuprates and heavy fermion systems [1]. The strongly correlated electrons in many of these systems however have meant that most theoretical work has concentrated on parameterised models in which the electronic motion is treated rather simply. Another complementary approach however is to use an ab initio theory such as Time Dependent Density Functional Theory (TDDFT) [2] but apply it to materials where it can be expected to work i.e. where the effects of electron correlations are not so important, but which otherwise have important similarities to the systems in question. For example with its perovskite structure containing transition metal(TM)-oxygen planes, Sr_2RuO_4 has several aspects in common with the HTC materials. But the presence of the 4d TM Ru rather than the narrower band 3d TM Cu means that electron correlation effects are smaller and therefore DFT-based calculations can provide a valuable starting point. Moreover its p-wave superconductivity at low temperature seems likely to be affected by spin fluctuations [3, 4, 5]. Concerning another example, the transition temperature separating paramagnetic and magnetically ordered phases of the cubic transition metal compound $MnSi$, which has the B20 crystal structure, is driven down to zero temperature upon the application of pressure. In the vicinity of the critical pressure for this quantum phase transition the system exhibits non- or marginal Fermi liquid properties [6].

With the objective of investigating the spin-fluctuations in nearly magnetic materials such as these we have recently devised and proven a new scheme for calculating the wave-vector and

frequency dependent dynamic spin susceptibility of metallic systems [7] which is based on the Time Dependent Density Functional Theory (TDDFT) of Gross et al. [2] and as such is an all electron theory. This enables the temperature dependent dynamic spin susceptibility of metals and compositionally disordered alloys to be calculated. In this article we outline the scheme and describe briefly some of our results for systems which although structurally and compositionally simpler than the two mentioned above, are also close to magnetic phase transitions.

Theoretical models in which an effective action for the slow spin fluctuations is written down have contributed greatly to our understanding of the properties of itinerant electron systems close to magnetic order [6]. Recent work which can incorporate results from DFT-based 'Fixed Spin Moment' (FSM) electronic structure calculations, treats these fluctuations classically [8]. A Landau-Ginzburg-like energy functional is written down, a free energy constructed which includes terms describing the interactions between the fluctuations (the mode-mode coupling) and properties such as the static susceptibility, specific heat and resistivity calculated. The FSM electronic structure calculations can be used to determine the coefficients in this functional [8]. Many informative studies have been carried out. For those calculations with such a DFT basis, these still remain qualitative investigations because of the lack of a prescription for the effective number of modes to include in the theory and its variation with temperature [6]. Stoner single particle excitation effects are also largely ignored. Both these issues can be addressed by the development and application of methods to calculate the temperature dependent dynamic paramagnetic spin susceptibility of nearly magnetic materials. The development of dynamic susceptibility calculations is particularly pertinent now that inelastic neutron scattering experiments, such as the time of flight measurements, have developed to the extent that spin fluctuations in nearly magnetic metals can be accurately measured [9].

Over the past few years great progress has been made in establishing TDDFT [2]. Analogs of the Hohenberg-Kohn [10] theorems of the static density functional (DFT) formalism have been proved and rigorous properties found. By considering a paramagnetic metal subjected to a small, time-dependent external magnetic field, $\mathbf{b}(\mathbf{r},t)$ which induces a magnetisation $\mathbf{m}(\mathbf{r},t)$ and using TDDFT in [7] an expression for the dynamic paramagnetic spin susceptibility $\chi(\mathbf{q},w)$ via a variational linear response approach can be derived [11]. Accurate calculations of dynamic susceptibilities from this basis have been scarce (e.g. [12]) because they are difficult and computationally demanding. In ref.[7] we showed that these problems can be mitigated by accessing $\chi(\mathbf{q},w)$ via the corresponding *temperature* susceptibility $\bar{\chi}(\mathbf{q},w_n)$ where w_n denotes a bosonic Matsubara frequency [13].

The dynamical spin susceptibility $\chi(\mathbf{q},w)$.

The equilibrium state of a paramagnetic metal, described by standard DFT, has density $\rho_0(\mathbf{r})$ and its magnetic response function

$$\chi(\mathbf{r}t;\mathbf{r}'t') = \frac{\delta m[b](\mathbf{r},t)}{\delta b(\mathbf{r}',t')}|_{b=0,\rho_0} \tag{1}$$

is given by the following Dyson-type equation.

$$\chi(\mathbf{r}t;\mathbf{r}'t') = \chi_s(\mathbf{r}t;\mathbf{r}'t') + \int d\mathbf{r}_1 \int dt_1 \int d\mathbf{r}_2 \int dt_2 \chi_s(\mathbf{r}t;\mathbf{r}_1t_1)K_{xc}(\mathbf{r}_1t_1;\mathbf{r}_2t_2)\chi(\mathbf{r}_2t_2,\mathbf{r}'t') \tag{2}$$

χ_s is the magnetic response function of the Kohn-Sham non-interacting system with the same unperturbed density ρ_0 as the full interacting electron system, and

$$K_{xc}(\mathbf{r}t;\mathbf{r}'t') = \frac{\delta b_{xc}(\mathbf{r},t)}{\delta m(\mathbf{r}',t')}|_{b=0,\rho_0} \tag{3}$$

is the functional derivative of the effective exchange-correlation magnetic field with respect to the induced magnetisation. As emphasised in ref.[2] eq.1 represents an exact representation of the linear magnetic response. The corresponding development for systems at finite temperature in thermal equilibrium has also been described [11]. In practice approximations to K_{xc} must be made and this work employs the adiabatic local approximation (ALDA) [2] so that

$$\begin{aligned} K_{xc}^{ALDA}(\mathbf{r}t;\mathbf{r}'t') &= \frac{db_{xc}^{LDA}(\rho(\mathbf{r},t),m(\mathbf{r},t))}{dm(\mathbf{r},t)}|_{\rho_0,m=0}\delta(\mathbf{r}-\mathbf{r}')\delta(t-t') \\ &= I_{xc}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\delta(t-t') \end{aligned} \tag{4}$$

On taking the Fourier transform with respect to time we obtain the dynamic spin susceptibility $\chi(\mathbf{r},\mathbf{r}';w)$.

For computational expediency we consider the corresponding *temperature* susceptibility [13] $\bar{\chi}(\mathbf{r},\mathbf{r}';w_n)$ which occurs in the Fourier representation of the temperature function $\bar{\chi}(\mathbf{r}\tau;\mathbf{r}'\tau')$ that depends on imaginary time variables τ,τ' and w_n are the bosonic Matsubara frequencies $w_n = 2n\pi k_B T$. Now $\bar{\chi}(\mathbf{r},\mathbf{r}';w_n) \equiv \chi(\mathbf{r},\mathbf{r}';iw_n)$ and an analytical continuation to the upper side of the real w axis produces the dynamic susceptibility $\chi(\mathbf{r},\mathbf{r}';w)$.

We can define a general system as having a crystal structure with lattice vectors $\{\mathbf{R}_i\}$ and where there are N_s non-equivalent atoms per unit cell. On the l^{th} of the N_s sublattices there are N_l possible atomic species with concentrations c_{α_l} $(\alpha_l = 1,\cdots,N_l)$. In each unit cell the N_s atoms are situated at locations $\mathbf{a}_l, l = 1,\cdots,N_s$. On carrying out a lattice Fourier transform over the lattice vectors $\{\mathbf{R}_i\}$ we obtain the following Dyson equation for the temperature susceptibility

$$\begin{aligned} \bar{\chi}^{\alpha_l}(\mathbf{x}_l,\mathbf{x}'_{l'},\mathbf{q},w_n) &= \sum_{\gamma_{l'}}^{N_{l'}} \bar{\chi}_s^{\alpha_l\gamma_{l'}}(\mathbf{x}_l,\mathbf{x}'_{l'},\mathbf{q},w_n) \\ &+ \sum_{l''}^{N_s} \int d\mathbf{x}''_{l''} \sum_{\gamma_{l''}}^{N_{l''}} \bar{\chi}_s^{\alpha_l\gamma_{l''}}(\mathbf{x}_l,\mathbf{x}''_{l''},\mathbf{q},w_n) I_{xc}^{\gamma_{l''}}(\mathbf{x}''_{l''}) \bar{\chi}^{\gamma_{l''}}(\mathbf{x}''_{l''},\mathbf{x}'_{l'},\mathbf{q},w_n) \end{aligned} \tag{5}$$

with $\mathbf{x}_l$,$\mathbf{x}'_{l'}$ and $\mathbf{x}''_{l''}$ measured relative to atomic cells centred on $\mathbf{a}_l$, $\mathbf{a}_{l'}$ and $\mathbf{a}_{l''}$ respectively.

In terms of the lattice Fourier transform of the DFT Kohn-Sham Green function of the static unperturbed system

$$\begin{aligned} &\bar{\chi}_s^{\alpha_l\gamma_{l'}}(\mathbf{x}_l,\mathbf{x}'_{l'},\mathbf{q},w_n) = \\ &-\frac{1}{\beta}\sum_m \int \frac{d\mathbf{k}}{v_{BZ}} \langle G(\mathbf{x}_l,\mathbf{x}'_{l'},\quad \mathbf{k},\mu+i\nu_m)\rangle_{\alpha_l\gamma_{l'}} \quad \langle G(\mathbf{x}'_{l'},\mathbf{x}_l,\mathbf{k}+\mathbf{q},\mu+i(\nu_m+w_n))\rangle_{\gamma_{l'}\alpha_l} \end{aligned} \tag{6}$$

where the integral is over the Brillouin zone of the lattice and $\mathbf{k}$, $\mathbf{q}$ and $\mathbf{k}+\mathbf{q}$ are all wavevectors within this Brillouin zone which has volume v_{BZ}. μ is the chemical potential and ν_m is a fermionic Matsubara frequency $(2n+1)\pi k_B T$. $\langle\cdots\rangle_{\alpha_l\gamma_{l'}}$ denotes an average over all configurations which have one site on sublattice l occupied by an α_l type of atom and another on sublattice l' occupied by a $\gamma_{l'}$ atom.

The Green function can be obtained within the framework of multiple scattering (KKR) theory [14] and this makes this formalism applicable to disordered alloys as well as ordered compounds and elemental metals, the disorder being treated by the Coherent Potential Approximation (CPA) [15].

To solve equation (5), we use a direct method of matrix inversion in which, for example, $\bar{\chi}_s$ is cast into matrixform of order $(\sum_{l=1}^{N_s} S_l N_l) \times (\sum_{l=1}^{N_s} S_l N_l)$ where S_l is the number of spatial grid points associated with an atomic cell on the l^{th} sublattice. Local field effects are thus fully incorporated. The full Fourier transform can then be constructed.

The most computationally demanding parts of the calculation are the convolution integrals over the Brillouin Zone which result from the expression for $\bar{\chi}_s$, eq. (6). Since all electronic structure quantities are evaluated at complex energies z, these convolution integrals have no sharp structure and can be evaluated straightforwardly by an application of the adaptive grid method of E.Bruno and B.Ginatempo [16] which has been found to be very efficient and accurate. In this method one can preset the level of accuracy of the integration by supplying an error parameter ϵ.

Once the temperature susceptibility $\bar{\chi}(\mathbf{q}, \mathbf{q}; w_n)$ has been calculated the dynamic susceptibility can be found. As discussed in ref. [13], for example, we can define the retarded response function $\chi(\mathbf{q}, \mathbf{q}, z)$ of a complex variable z. Since it can be shown [13] formally that $\lim_{z\to\infty} \chi(z) \sim 1/z^2$ and we can obtain $\chi(iw_n)$ from the above analysis it is possible to continue analytically to values of z just above the real axis, i.e. $z = w + i\eta$. In order to achieve this we fit our data to a rational function

$$\bar{\chi}(\mathbf{q}, \mathbf{q}, w_n) = \chi(\mathbf{q}) \frac{(1 + \sum_{k=1}^{M-2} U_k(\mathbf{q}) w_n^k)}{(1 + \sum_{k=1}^{M} D_k(\mathbf{q}) w_n^k)} \tag{7}$$

in which M is an even integer. This form *ensures* that the sum rule involving the static susceptibility $\chi(\mathbf{q})$ is satisfied, i.e.

$$\chi(\mathbf{q}) = \frac{2}{\pi} \int_0^\infty dw \frac{Im\chi(\mathbf{q}, \mathbf{q}, w)}{w} \tag{8}$$

We find that very good fits are obtained with small M for a wide range of w_n's, $M = 4$ for Pd whereas for Cr and its dilute alloys $M = 2$ making the analogy with an overdamped harmonic oscillator model very close.

Antiferromagnetic paramagnons in Cr and its dilute alloys.

This new scheme has been demonstrated very recently by an investigation into the nature of the spin fluctuations in paramagnetic Cr and compositionally disordered $Cr_{95}V_5$ and $Cr_{95}Re_5$ alloys with good agreement with experimental data [7]. For example, recent inelastic neutron scattering experiments [17, 9] have measured incommensurate AF 'paramagnons', persisting up to high frequencies in $Cr_{95}V_5$ which were also shown in our calculations.

Chromium is the archetypal itinerant anti-ferromagnet (AF) whose famous incommensurate spin density wave (SDW) ground state is determined by the nesting wave-vectors $\mathbf{q}_{nest}$ identified in the Fermi surface [17]. Chromium alloys also have varied AF properties [17] and their paramagnetic states have recently attracted attention owing, in part, to analogies drawn with the high temperature superconducting cuprates especially $(La_cSr_{1-c})_2CuO_4$ [17]. For example,

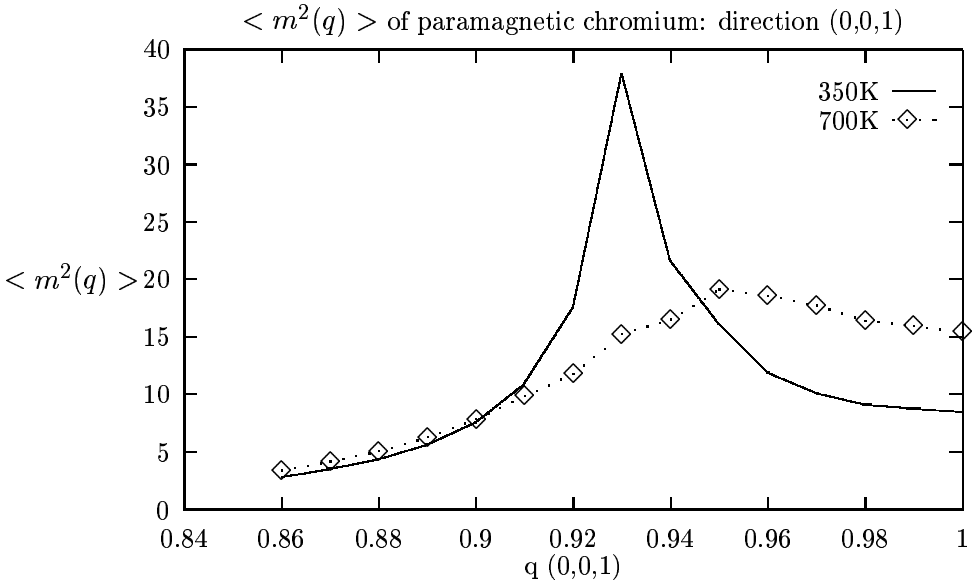

Figure 1: The variance of the spin fluctuations in paramagnetic Cr $< m^2(\mathbf{q}) >$ in μ_B^2 for wave-vectors $\mathbf{q}$ along the $\{0,0,1\}$ direction at 350K (full line) and 700K (dotted).

$Cr_{95}Mn_5$ or $Cr_{95}Re_5$ are simple commensurate AF materials which on lowering the electron concentration by suitable doping develop incommensurate spin fluctuations promoted by imperfectly nested Fermi surfaces. In [7] we explored the temperature dependence, variation with dopant concentration and the evolution of the spin fluctuations in these systems from incommensurability to commensurability with increasing frequency and provided the first ab-initio description of these effects [7]. Although there have been several simple parameterised models to describe the magnetic properties of Cr and its alloys [17], these have all concentrated on the approximately nested electron 'jack' and slightly larger octahedral hole pieces of the Fermi surface [17] and, at best, have only included the effects of all the remaining electrons via an electron reservoir. Whilst finding similarities between our results and results from such models we showed that a complete picture is obtained only when an electronic band-filling effect which favours a simple AF ordering at low temperature is also considered. We also found that the spin fluctuations are given an accurate description as overdamped diffusive simple harmonic oscillator modes which are at the heart of theories of the effects of spin fluctuations upon the properties of itinerant electron systems [6].

The nature of the spin fluctuations can be succinctly described via the variance $< m^2(\mathbf{q}) >$. From the fluctuation dissipation theorem, $< m^2(\mathbf{q}) >= (1/\pi) \int_{-\infty}^{\infty} dw (1 - \exp(-\beta w))^{-1} Im\chi(\mathbf{q}, \mathbf{q}, w)$. Fig.1 shows $< m^2(\mathbf{q}) >$ at two temperatures for Cr where we have used a frequency cutoff of 500 meV and so have not included the faster of the quantum fluctuations. Near T_N the magnetic fluctuations have their greatest weight around the $\mathbf{q}_{nest}$. At higher T the peak diminishes and weight grows at $\mathbf{q}$'s nearer $\{0,0,1\}$ reflecting the shift in the peak in $Im\chi(\mathbf{q}, \mathbf{q}, w)$ from $\mathbf{q}_{nest}$ to commensurate $\mathbf{q}$'s with increase in frequency w.

The paramagnons of nearly ferromagnetic Pd.

We finish this article with a brief examination of the timescales associated with the spin fluctuations of Pd, a 4d transition metal so close to being a ferromagnet. Much has been written

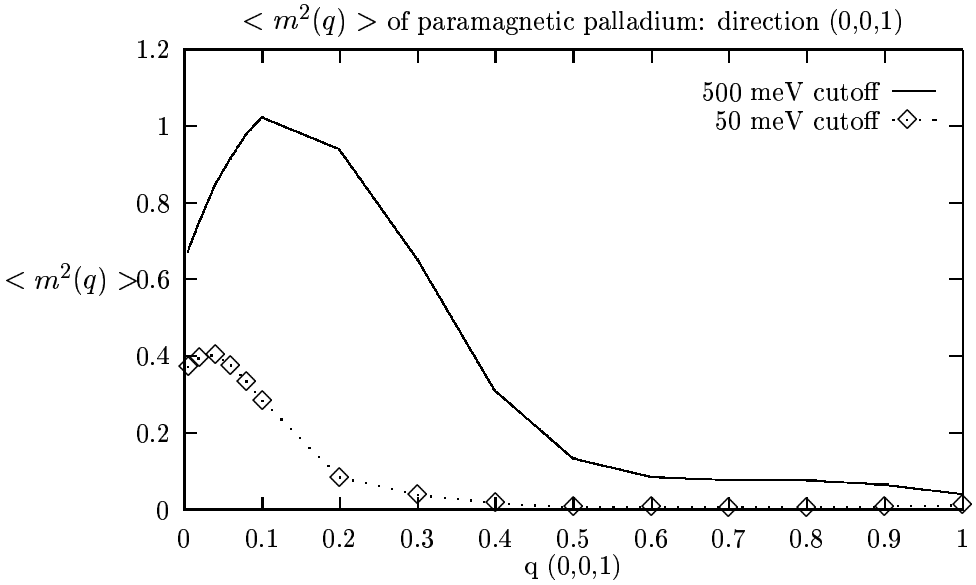

Figure 2: $< m^2(\mathbf{q}) >$ for wave-vectors $\mathbf{q}$ along $\{0, 0, 1\}$ in Pd at 100K with a frequency cutoff 500 meV (full line) and 50 meV (dotted).

about the low temperature spin fluctuations in this 4d transition metal especially those slow modes with long wavelength and in the context of possible p-wave superconductivity mediated by ferromagnetic paramagnons [18]. Fig.2 shows the magnetic correlations $< m^2(\mathbf{q}) >$ for Pd at 100K calculated using energy cutoffs of 500meV and 50meV. The paramagnons are clearly visible for a narrow region of small wave-vectors $\mathbf{q}$.

Acknowledgements JP acknowledges support from the Thailand Research Fund contract RTA/02/2542 and BG and JBS from the TMR Research Network on 'Electronic Structure Calculations of Materials Properties and Processes for Industry and Basic Sciences'.

References

[1] S.Sachdev, Physics World, **12**, no.4,33, (1999); R.B.Laughlin, Adv.Phys. **47**,943, (1998)

[2] E.Runge et al., Phys.Rev.Lett. **52**, 997, (1984); E.K.U.Gross et al., Phys.Rev.Lett. **55**, 2850, (1985); E.K.U.Gross et al. in 'Density Functional Theory', ed. R.F.Nalewajski, Springer Series 'Topics in current Chemistry' (1996).

[3] A.P.Mackenzie et al., Phys.Rev.Lett. **80**, 161, (1998); T.M.Rice and M.Sigrist, J.Phys.Condens. Matter **7**, L643, (1995).

[4] I.I.Mazin and D.J.Singh, Phys.Rev.Lett. **79**, 733, (1997), I.I.Mazin and D.J.Singh, Phys.Rev.Lett. **82**, 4324 (1999).

[5] P.Monthoux and D.Pines, Phys.Rev.Lett. **69**, 961, (1992); P.Monthoux and G.G.Lonzarich, Phys.Rev. B**59**, 14598, (1999).

[6] e.g. G.G.Lonzarich, ch.6 in 'Electron a centenary volume', ed. M.Springford, C.U.P., (1997); S.Julian et al., J.Phys.: Condens. Matter, **8**, 9675, (1996); J.A.Hertz, Phys.Rev.B **14**, 7195, (1976); A.J.Millis, Phys.Rev.B **48**, 7183, (1993).

[7] J.B.Staunton, J.Poulter, B.Ginatempo, E.Bruno and D.D.Johnson, (1999), Phys.Rev.Lett. **82**, 3340-3343.

[8] D.Wagner, J.Phys.CM **1**, 4635, (1989); P.Mohn and K.Schwarz, J.Mag.Magn.Mat. **104**, Pt1, 685, (1992); M.Uhl and J.Kubler, Phys.Condens.Matter **9**, 7885, (1997)

[9] R.Doubble et al., Physica B **237**, 421, (1997). R.Doubble, PhD Thesis, University of Bristol, (1998).

[10] P.Hohenberg and W.Kohn, Phys.Rev. **136**, B864, (1964); W.Kohn and L.J.Sham, Phys.Rev.**140**, A1133, (1965).

[11] T.K.Ng and K.S.Singwi, Phys.Rev.Lett. **59**,2627, (1987); W.Yang, Phys.Rev.A **38**,5512,(1988); K.Liu et al., Can.J.Phys. **67**, 1015, (1989).

[12] e.g. E.Stenzel et al., J.Phys.F **16**,1789, (1986); S.Y.Savrasov, Phys.Rev.Lett. **81**, 2570, (1998).

[13] A.L.Fetter and J.D.Walecka, 'Quantum Theory of Many Particle Systems', (McGraw-Hill), (1971).

[14] J.S. Faulkner and G.M. Stocks, Phys.Rev.B **21**, 3222, (1980).

[15] P.Soven, Phys.Rev.**156**, 809, (1967); G.M.Stocks et al. Phys.Rev.Lett. **41**, 339, (1978); G.M.Stocks and H.Winter, Z.Phys.B **46**, 95, (1982); D.D.Johnson et al., Phys.Rev. B**41**, 9701 (1990).

[16] E.Bruno and B.Ginatempo, Phys.Rev. B**55**, 12946, (1997).

[17] E.Fawcett, Rev.Mod.Phys.**60**, 209, (1988); E.Fawcett et al., Rev.Mod.Phys.**66**, 25, (1994)

[18] D.Fay and J.Appel, Phys.Rev.B **22**, 3173, (1980).