

## A calculation of the Coulomb correlation energy, $U$ , for transition metals in Hubbard's model

To cite this article: B N Cox *et al* 1974 *J. Phys. F: Met. Phys.* **4** 807

View the [article online](#) for updates and enhancements.

### You may also like

- [A selfconsistent theory of localization](#)  
R Abou-Chakra, D J Thouless and P W Anderson
- [QuantumATK: an integrated platform of electronic and atomic-scale modelling tools](#)  
Søren Smidstrup, Troels Markussen, Pieter Vanraeyveld *et al.*
- [Strain effect on electronic structure and transport properties of zigzag  \$T\_3\$  nanoribbons: a mean-field theoretical study](#)  
Xing Cheng, Benhu Zhou, Benliang Zhou *et al.*

# A calculation of the Coulomb correlation energy, $U$ , for transition metals in Hubbard's model

B N Cox, M A Coulthard† and P Lloyd

Physics Department, Monash University, Clayton, 3168 Australia

Received 10 August 1973, in final form 15 October 1973

**Abstract.** The intra-atomic electron-electron Coulomb correlation energy  $U$ , which appears in the Hubbard Hamiltonian, is shown to be well approximated by the change in eigenvalue of a localized Hartree-Fock state that occurs when the occupation of that state is changed. A selfconsistent calculation of all the Hartree Fock states within a neutral Wigner-Seitz cell is made for three electronic configurations of each of the transition metals. Values of  $U$  are deduced from the differences in the d electron eigenvalues of the configurations. It is found that the ratios  $U/W$ , where  $W$  is the bandwidth, show a trend across the transition metals which is in excellent agreement with the known magnetic properties of the their ground states.

## 1. Introduction

One of the most studied and certainly the simplest model to describe correlation effects in metallic crystals is the Hubbard model (Hubbard 1963, 1964a, 1964b, 1965, 1966). For simplicity this model was originally formulated as if the conduction electrons were all contained in a single narrow s band, and it is in this form that the model has been extensively studied (see the conference report on the Hubbard Hamiltonian 1968). The model is, however, not limited to such a system and may be used in the more realistic situation in which the electrons occupy a degenerate metallic d band (Siegel and Kemeny 1972, Siegel 1973), and indeed the model was originally introduced to study the properties of d bands in transition metals. A general formulation of the model is begun by introducing a complete set of atomic orbitals which we shall label ' $\alpha$ '. Such orbitals may be used in a tight binding calculation, and a one electron tight binding Hamiltonian is obtained if only the energy  $\epsilon_\alpha$  of each orbital and the overlap integrals between the orbitals on atom  $i$  and atom  $j$ ,  $V_{i\alpha j\alpha'}$ , are retained. However the Hubbard Hamiltonian was specifically intended for the study of correlation effects, and consequently the intra-atomic electron-electron interaction,  $U$ , is included. In practice and in the present calculation,  $U$  embraces only the interactions between two d orbital electrons on the same atomic site. If the degenerate d orbitals are labelled  $\mu, \nu, \sigma, \tau \dots$ , then the Hamiltonian has the model form

$$H = \sum_i \left( \sum_\alpha \epsilon_\alpha n_{i,\alpha} + \frac{1}{2} \sum_{\substack{\mu, \nu \\ \sigma, \tau}} U C_{i,\mu}^+ C_{i,\nu}^+ C_{i,\tau} C_{i,\sigma} \right) + \sum_{\substack{i, \alpha \\ j, \alpha'}} V_{i,\alpha,j,\alpha'} C_{i,\alpha}^+ C_{j,\alpha'} \quad (1.1)$$

† Now at: CSIRO, Division of Applied Geomechanics, PO Box 54, Mt. Waverley, 3149 Australia.

Although the model was originally meant for the study of transition metals, its most realistic application has been to transition metal oxides and other such narrow band materials (Adler 1968, 1970, Mott and Zinamon 1970). The purpose of this paper is to calculate a numerical value of the electron–electron interaction,  $U$ , which may be used in either context.

The common conclusion of analyses of the model is the prediction of a transition from a normal band structure to a split band if  $U \sim W$ , the bandwidth, and it has been shown that such a transition is a consequence of the model by Cyrot (1972a). The value of the ratio  $U/W$  at which this transition occurs has been the subject of a great amount of work; this work has been reviewed in the references above and some recent calculations have been made by Ikeda *et al* (1972), Cyrot (1972b) and Johansson (1973). The transition causes the material to change from a metal to an insulator, or from a non-magnetic material into a magnetic one, and these features of the model may be considered to be reasonably well understood. However, in spite of the large amount of work which has been expended on this model, there has been little progress made towards actually estimating the numerical values of  $U$  which may be expected to occur in real systems. These are important because the whole success of the Hubbard Hamiltonian depends on correctly choosing the electron–electron interaction energy parameter.

The analytic expressions giving the matrix elements  $U$  in equation (1.1) in terms of fundamental quantities are contained in all the textbooks on many particle theory (eg Thouless 1961). In the standard formalism, which is the formalism which has been used either directly or indirectly ever since the first Hubbard paper in 1963, the creation operator  $C_{i,\mu}^+$  creates (in configurational space) a well defined single particle atomic orbital, say  $\phi_\mu(\mathbf{r} - \mathbf{R}_i)$ , on the crystal site  $i$ . The electrostatic energy between two such orbitals is

$$U_{\mu,\nu} = \int d^3r' \int d^3r |\phi_\mu(\mathbf{r})|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} |\phi_\nu(\mathbf{r}')|^2. \quad (1.2)$$

and this appears to give a well defined value of  $U$ .

In addition to this energy there is also an exchange term, but we shall ignore this term as it is normally considerably smaller than the direct Coulomb term. It should be clearly noted that if this definition is taken at its face value and evaluated directly, it gives, over a wide range of different shapes for the atomic orbitals, a value for the interaction energy  $U$  of about 20 eV. Such a value causes unacceptable disagreement between the model's predictions and experimental observations.

This failing was realized quite early and it was suggested that the electron–electron interaction energy had to be 'screened', so that the value given by the definition (1.2) is not the value of  $U$  which appears in the Hubbard Hamiltonian. An early estimate by Herring (1966) suggested that the screened value might be as low as 0.5 eV, but a value as low as this is also in disagreement with the experimental results. In fact, very few attempts have been made to clarify the reason why the definition (1.2) is unacceptable. Instead values of  $U$  have been deduced experimentally, and when these values are used in the Hubbard Hamiltonian sensible results are obtained.

The optical spectra of free atoms have been used by Friedel (1969) in order to deduce a value for  $U$ . The spectral energy levels in atoms will be different in different configurations simply because of the electron–electron correlation energy, and hence a consideration of the transitions between different states of ionization allows an estimate of  $U$  to be made. This technique appears to be slightly marred by strong dependence on

the 4s shell occupation, and the difference between atomic and metallic d orbitals. By this method Friedel obtained an upper limit of 10 eV for  $U$  in nickel. The correlation energy is, of course, still present if the transition element is present as a dilute impurity in a simple metal and probably the best estimates of  $U$  have been obtained using photoemission results from the split virtual d levels of such impurities. These experiments are reviewed by Heeger (1969): they give a value of  $U$  which is nearly independent of the impurity concentration and is about 4 eV.

This paper presents an *a priori* calculation of the effective electron–electron interaction energy, the energy which should be used as an input parameter to the Hubbard model, for the d electrons of the transition metals. The full reasoning behind our calculation is given in §2, but in short we take the effective value of  $U$  to be the difference between the Hartree–Fock energy levels for a local d state in two different configurations of that atom. This is not a free atom calculation but is a Hartree–Fock cellular calculation with Wigner–Seitz boundary conditions. The details of this calculation are given in §3.

## 2. On defining $U$

Any elementary textbook on many body theory contains a section in which it is proven conclusively that a second quantized formalism such as the basic equation (1.1) of the Hubbard model (with the matrix elements defined analogously to (1.2)) is mathematically equivalent to the exact many particle Schrödinger equation in real space. At first sight, then, it would appear that (1.2) is a good definition of  $U$ , and that  $U$  should be of the order of 20 eV, even if this does disagree with experimental results. This is not correct. The equivalence of the second quantized form and the configurational space representation of the Schrödinger equation depends on the use of a complete orthonormal set of states in the second quantized form, whereas the whole point of the Hubbard model is that only a very restricted set of orbitals is actually included. This is exactly the reason why the Hubbard model has been so widely studied: it is hoped that this simplified model still retains the physically important features of the real problem without having the complications of the exact Hamiltonian. When the entire set of the orthonormal basis states is not included in (1.1), then equation (1.2) no longer defines the ‘best’ value of the parameter  $U$ . This value must be changed (‘renormalized’) in order to allow for the fact that the model Hamiltonian precludes any virtual transitions to these excluded states. It is the modifications to the wavefunctions which result from these virtual transitions to the excluded states which would ‘screen’ the value of  $U$  if they had been included. Formal expressions for the elimination of any given set of states from a Hamiltonian and the Schrödinger equation may be easily written down, but we shall not do so here. However, it should be noted that the value of  $U$  which is calculated to be the best input parameter for the Hubbard model should only include the screening from the excluded states and should not include any effects which result from solving the Hubbard Hamiltonian itself.

In a Hartree–Fock calculation of the energy levels of a free atom similar considerations apply in that only one orbital per electron is included in the Slater determinantal wavefunction. In different configurations of the atom a Hartree–Fock calculation predicts different single particle energy levels, which is directly due to the electron–electron interaction. Moreover, these calculated levels are in good agreement with the observed spectral energy levels, especially on the scale of errors commonly tolerated in solid state physics. The Hartree–Fock calculation allows for the virtual transitions to

excluded orbitals by allowing the single particle orbitals themselves to alter with the electronic configuration. Unlike the formal theory of second quantization a selfconsistent theory such as the Hartree–Fock method allows the single particle states to vary with their occupation, and in our calculation a similar idea is used in order to make allowance for the excluded virtual transition.

We have performed a relativistic Hartree–Fock calculation for the elements of the first row of the transition metal series (Sc → Ni) with boundary conditions being chosen to be appropriate to an atom contained in a metallic crystal. The boundary conditions assume that the atom is entirely contained by a spherical cell whose volume equals that of the atom in the metal, as in the approach of Wigner and Seitz (1933). The boundary conditions on the surface of the cell are also those of Wigner and Seitz, heuristically modified for a relativistic calculation. The validity and nature of this method has been discussed at length for the nonrelativistic case by Brooks (1958). It might be noted that such a calculation is entirely structure independent, because only the volume of the cell enters into the calculation and not the crystal structure or even whether the structure is crystalline. Our results show that the value of  $U$  obtained is fairly insensitive to the radius of the cell and therefore should be applicable to materials other than just the pure metal. On the other hand these boundary conditions certainly alter the eigenvalues from those of a free atom (Watson 1960, Abdulnur *et al* 1972).

In this local calculation the states ‘relax’ according to the configuration of the cell and thereby make allowance for the orbitals excluded from the Hubbard Hamiltonian. This alteration of the orbitals with the occupation of the cell implies that the creation and destruction operators in the second quantized formalism,  $C_x^+$  and  $C_x$ , are no longer associated with some unique orbital,  $\phi_x(\mathbf{r})$  in configurational space, as is usually assumed. The occupation of a Slater determinant is changed by such an operator, but at the same time all the other individual orbitals are correspondingly changed. Fortunately, the formal definition of the creation and destruction operators in terms of single particle orbitals is inessential to the validity of all the previous studies of the Hubbard model. What is essential is that the algebraic relations between these operators should remain the same. It is shown in the appendix that the commutation relations between the creation and destruction operators may be defined in terms of an occupation number Fock space formalism, and that the states with a given occupation number do not actually have to be Slater determinants at all.

Historically two local environment or cellular methods have been used in solid state physics. One of these is the Wigner–Seitz method which we have used and the other is the ‘renormalized atom’ approach of Chodorow (1939) (see also Segall 1962 and Berggren 1972). In the latter approach the free atom wavefunction is unmodified in shape but cut off at the Wigner–Seitz radius and then multiplied by a scaling constant to give it the correct normalization. This approach has been used recently by Hodges *et al* (1972) for transition metals and by Herbst *et al* (1972) for rare earth metals. In the latter calculation a value of  $U = 7 \text{ eV}$  was obtained. (The former calculation was not directly related to the Hubbard model.) We would like to make the following comment here on this technique. Hodges *et al* found that the position of the d level was shifted upwards in value from its free atom value, in disagreement with many previous assumptions. The renormalized atom approach corresponds to the first iteration in our self-consistent Hartree–Fock calculation, and we also found this effect. However, on further iterations of the Hartree–Fock scheme towards selfconsistency it was found that the d levels shifted back towards the free atom values again. It is possible that the renormalized atom approach contains some element of physical reality that we have not

captured by a relativistic selfconsistent calculation employing Wigner–Seitz boundary conditions, but our calculations indicate a value for the d electron energy level closer to the free atom value than does the renormalized atom approach.

Consider now the occupation number Hamiltonian for a single Wigner–Seitz cell. Let

$$\Delta_{\alpha} = n_{\alpha} - \langle n_{\alpha} \rangle_0 \quad (2.1)$$

be the deviation of the occupation of the level  $\alpha$  from the expectation value of equilibrium  $\langle n_{\alpha} \rangle_0$ . A simple effective Hamiltonian is then

$$H = E_0 + \sum_{\alpha} \epsilon_{\alpha} \Delta_{\alpha} + \frac{1}{2} \sum_{\alpha, \alpha'} U_{\alpha\alpha'} \Delta_{\alpha} \Delta_{\alpha'} + \dots \quad (2.2)$$

In practice the interaction term  $U_{\alpha\alpha'}$  was taken to be nonzero only for electrons in the d orbitals as the calculation showed that the 4s eigenvalues altered by at most 0.1 eV when the neutral atom configuration was changed. For the reference state  $|\Delta_{\alpha} = 0\rangle$

$$H|\Delta_{\alpha} = 0\rangle = E_0|\Delta_{\alpha} = 0\rangle \quad (2.3)$$

and hence  $E_0$  is the total energy of the ground state configuration. In principle the other coefficients could be obtained by calculating the total energy of other configurations for which  $\Delta_{\alpha} \neq 0$ , and then fitting these results to the effective Hamiltonian (2.2). However, in a metal the 4s electrons are spread over quite wide energy bands whereas our method above represents them all as being in a single orbital whose energy is normally assumed to be the bottom of the conduction band. If the total energy is to be used, then a correction for this must be made. This was the approach of Herbst *et al* (1972) when they calculated the value of  $U$  for the rare earth metals; however, as far as the present calculation is concerned we felt that the magnitude of the correction was so much larger than the effect being sought that such an approach would be quite inaccurate.

On the other hand the effect of the 4s electrons on the d eigenvalue is expected to be quite small and consequently we estimated  $U$  from the single particle eigenvalues rather than from the total energy. The single particle eigenvalue is given in terms of the effective Hamiltonian (2.1) by

$$\frac{\delta H}{\delta \Delta_{\alpha}} = \epsilon_{\alpha} + \sum_{\beta} U_{\alpha\beta} \Delta_{\beta} + \dots \quad (2.4)$$

Hence if  $\Delta_{\alpha} = 0$  for all  $\alpha$  the eigenvalue is  $\epsilon_{\alpha}$ , while if the occupation is altered by one unit in the state  $\alpha_0$  the eigenvalue is changed to  $\epsilon_{\alpha} \pm U_{\alpha\alpha_0}$ . The value of  $U$  may be estimated from the change in the eigenvalue.

### 3. The calculation

The one electron eigenstates and eigenvalues for a configuration of electrons at a local site were calculated in a selfconsistency seeking iterative procedure using a computer program. The local site was defined by a sphere whose volume was equal to the volume of the atom in the crystal. The radius of the sphere, the Wigner Seitz radius, was deduced from the crystallographic tables of Wyckoff (1948). The Wigner–Seitz radii used for the calculations are shown in figure 1.

The configurations used were chosen to maintain the charge neutrality of the sphere. Therefore, the three available configurations for each metal were  $3d^n 4s^1$ ,

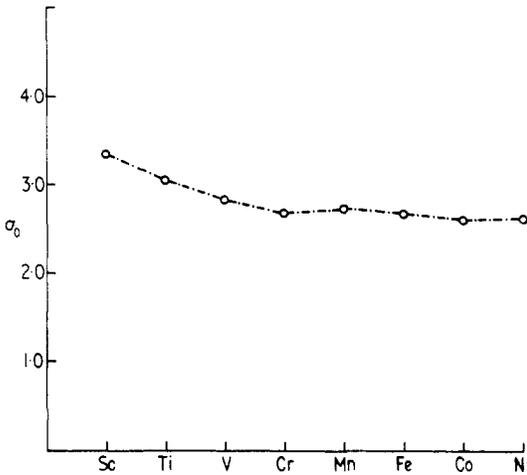


Figure 1. The Wigner-Seitz radius used for each calculation. The variation in  $r_{ws}$  among different stable structures that may exist for any particular metal is of the order of 1%.

$3d^{n-1}4s^2$ , and  $3d^{n+1}4s^0$ . The selfconsistent one electron eigenenergies were obtained for each of these configurations.

The program itself was a slight modification of one developed by Coulthard (1967, 1973) for the free atom. This was a relativistic Hartree-Fock calculation for the average of configuration (Grant 1970), with magnetic interactions and off diagonal lagrange parameters omitted. In fact, the only alterations which were made to the free atom program were to substitute a grid which extended only to the Wigner-Seitz radius and to include boundary conditions at the sphere's surface. The boundary conditions are described below.

The eigensolutions of the spherically symmetric relativistic one electron Hamiltonian can be written (Grant 1970)

$$\psi_{A,m_A}(\mathbf{r}) = \begin{bmatrix} \frac{iP_{n_A,k_A}(r)}{r} \chi_{k_A,m_A}(\theta, \phi) \\ \frac{Q_{n_A,k_A}(r)}{r} \chi_{-k_A,m_A}(\theta, \phi) \end{bmatrix} \quad (3.1)$$

The relativistic quantum numbers  $|n_A, k_A, m_A\rangle$  are used to describe a one-electron state. The function  $\chi(\theta, \phi)$  is a known spin-orbit eigenfunction, while the radial eigenfunctions  $P_A(r)$  and  $Q_A(r)$  are calculated in the computer program. It was found that the minor part  $Q_A(r)$  was typically of the order of a tenth of  $P_A(r)$ . The  $(2l + 1)$ -fold degenerate nonrelativistic state  $|n, l\rangle$  is split in the relativistic case, for  $l > 0$ , into two states  $|n, k\rangle$  where

$$\begin{aligned} k &= l & \text{for } j &= l - \frac{1}{2} \\ k &= -(l + 1) & \text{for } j &= l + \frac{1}{2}. \end{aligned} \quad (3.2)$$

In particular, the tenfold degenerate nonrelativistic 3d state splits into two states,  $3d^-$  (for  $j = l - \frac{1}{2}$ ) and  $3d^+$  (for  $j = l + \frac{1}{2}$ ), which are respectively fourfold and sixfold degenerate. However, the difference in energy of these two states is quite small in our

case (see figure 2). Since the state  $3d^-$  is always lower in energy than the  $3d^+$  state, the former is always filled first in all the configurations. The unfilled state is then solved in the average of all possible spin and orbital angular momentum configurations.

Because the radial solution  $P_A(r)$  dominates the term involving  $Q_A(r)$ , it is appropriate to use boundary conditions on  $P_A(r)$  alone. The boundary conditions chosen were those derived by Brooks (1958) for the spherical cell model in the nonrelativistic case. They are

$$\left(\frac{dP_A}{dr}\right)_{r_{ws}} = \frac{P_A(r_{ws})}{r_{ws}} \quad \text{if } l \text{ is even} \tag{3.3a}$$

and

$$P_A(r_{ws}) = 0 \quad \text{if } l \text{ is odd.} \tag{3.3b}$$

(These boundary conditions have been used before in a relativistic Wigner-Seitz cell calculation for gold by Tucker *et al* (1969)). The functions  $P_A(r)$  and  $Q_A(r)$  were subject to the normalization condition

$$\int_0^{r_{ws}} [P_A(r)^2 + Q_A(r)^2] dr = 1. \tag{3.4}$$

The program was begun with starting potential functions calculated in one of two ways. Where they were available, previously calculated selfconsistent relativistic Hartree-Fock wavefunctions for the free atom were truncated at the Wigner-Seitz radius and renormalized and the first potential functions constructed from what resulted. The behaviour of the eigenvalue in this case is described at the end of this paragraph. If such free atom solutions were not available, then Hartree wavefunctions were calculated for an approximate potential, and the first potential functions constructed from these. The program was then run until the required selfconsistency was achieved. In fact after no more than ten iterations it was found that the d electron and conduction electron eigenvalues changed with a further iteration by less than 0.001 eV.

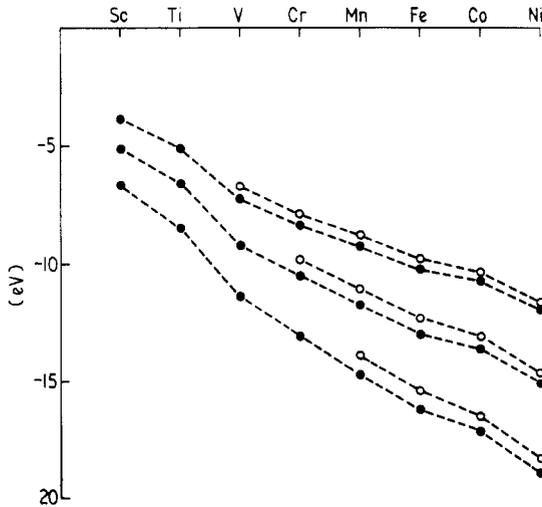


Figure 2. The  $3d^-$  and  $3d^+$  eigenvalues for each configuration. The lowest eigenvalues are for the  $3d^{n-1}4s^2$  configuration, the next are for the  $3d^n4s$  configuration, and the highest are for the  $3d^{n+1}$  configuration. ●  $3d^-$  state: ○  $3d^+$  state.

As it was noted in §2, the  $3d^-$  and  $3d^+$  eigenvalues did vary by large amounts in the early iterations. When the potential functions at the beginning of a run were constructed from truncated and renormalized free atom solutions, it was found, for manganese in the  $3d^5 4s^2$  configuration, that the  $3d^-$  and  $3d^+$  eigenvalues rose after the first iteration from their free atom values of  $-15.3$  eV and  $-14.4$  eV to  $-10.2$  eV and  $-9.5$  eV respectively. However, when selfconsistency was achieved the eigenvalues had returned to the values  $-14.7$  eV and  $-13.8$  eV respectively.

The calculated d eigenvalues for the different configurations are shown in figure 2. In this figure the black dot gives the eigenvalue for the  $j = l - \frac{1}{2}$  d state while the open dot gives the  $j = l + \frac{1}{2}$  state. The different configurations then have somewhat different values with the  $3d^{n+1} 4s^0$  having the highest eigenvalues, the  $3d^n 4s^1$  being the intermediate set and the  $3d^{n-1} 4s^2$  configuration having the lowest energies.

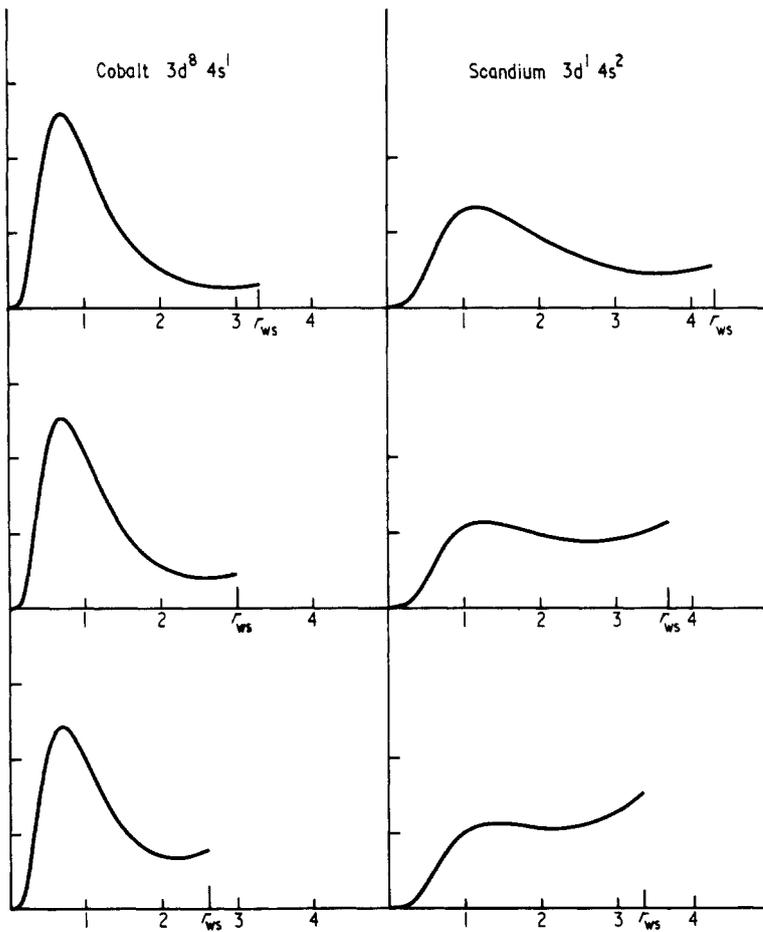


Figure 3. The  $3d^-$  wavefunctions for three values of  $r_{ws}$  for scandium in the  $3d^1 4s^2$  configuration and cobalt in the  $3d^8 4s^1$  configuration. The quantity  $(P(r)^2 + Q(r)^2)$  is plotted, which is proportional to the relative probability of finding the electron in an infinitesimal shell at radius  $r$ . Note that because the boundary condition is satisfied for the quantity  $P(r)/r$ , the curves are not flat at  $r_{ws}$ . Observe also that the height of the peak of each wavefunction is lowered as  $r_{ws}$  decreases.

The dependence of the results on the choice of Wigner-Seitz radius was investigated by repeating the calculations for several of the metals using various Wigner-Seitz radii. In general it was found that as  $r_{ws}$  was increased the greatest increase in the 3d eigenvalues occurred for the configuration  $3d^n4s^2$ . A smaller increase was observed for the configuration  $3d^n4s^1$ , while for the configuration  $3d^{n+1}4s^0$  nearly no change, or sometimes even a decrease, was found. The net effect on  $U$  was that it varied approximately linearly with the Wigner-Seitz radius. At first thought it would be expected that as the cell size increases the d eigenfunctions should become less concentrated, and thus the value of  $U$  should decrease. However, it was found that as the cell radius increased the wavefunctions actually became more compacted. This is shown for scandium and cobalt in figure 3, the curves being quite typical. It should be noted that, since the volume of the Wigner-Seitz cell varies as the cube of its radius,  $U$  has been found to vary quite slowly with the metallic density. Thus the values of  $U$  predicted by this calculation will be much the same for all phases and structures of any one metal.

#### 4. Conclusions

The difference between the different eigenvalues for the different configurations in figure 2 is due to the electron-electron interaction energy. This interaction energy will depend slightly on the actual configurations being considered: it will be different depending on whether the change in occupation occurs in a  $j = l - \frac{1}{2}$  shell or a  $j = l + \frac{1}{2}$  shell and it will be different if the number of electrons in the d-shell changes from  $3d^n4s^1$  to either  $3d^{n-1}4s^2$  or  $3d^{n+1}4s^0$ . In the Hubbard model only a single value of  $U$  is considered and so these slightly different values also were reduced to a single value here. For scandium and titanium the average of the only two possible differences was taken as the value of  $U$ . For vanadium the only change possible in the lowest energy configuration of the cell, which maintains the value of  $j$  (actually  $j = l - \frac{1}{2}$ ), is the  $3d^n4s^1$  to

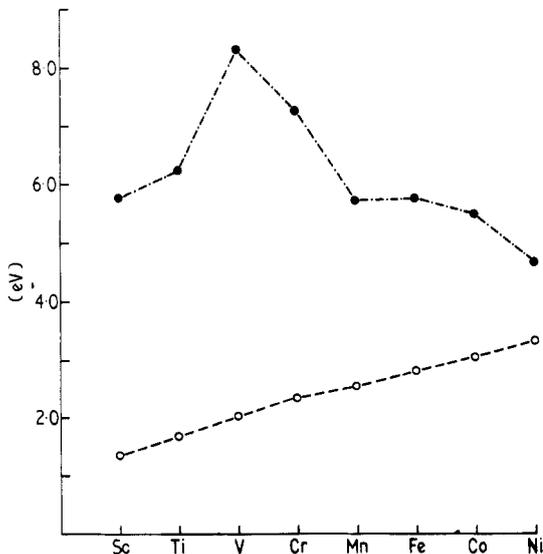


Figure 4. The values of  $U$  (○) obtained are plotted with the band widths,  $W$  (●), calculated by Fletcher and Nudel (1973).

$3d^{n-1}4s^2$ , and it was this change in eigenvalue that was taken as being  $U$ . Similarly for chromium only the change  $3d^{n+1}4s^0$  to  $3d^n4s^1$  was used. For the other elements the average value of the two possible changes of the  $j = l + \frac{1}{2}$  shell was taken. The results of this calculation are shown in figure 4.

The calculated values of  $U$  show a steady increase across the transition series, varying from 1.35 eV for scandium to 3.3 eV for nickel. This trend in  $U$  is to be expected on simple physical grounds: the d eigenvalue decreases strongly as one moves from scandium (with atomic number  $Z = 21$ ) to nickel (with  $Z = 28$ ) so that for the noble metal copper it is energetically favourable to fill completely the d shell. With this decrease in eigenenergy the d eigenfunction becomes successively more compacted inside the atomic cell and hence its electron-electron correlation energy increases. The trend is maintained for copper, for which we also calculated  $U$ , even though it is not a transition metal. For copper we obtained a value for  $U$  of 4.1 eV, which is considerably higher than the value for nickel.

Careful inspection of figure 4 reveals that the four values of  $U$  to the left of and including chromium lie on a nearly straight line, and likewise the four values to the right of and including manganese. Between chromium and manganese, however, there is a pronounced discontinuity. This is an effect of the splitting of the nonrelativistic tenfold degenerate 3d state into two relativistic states,  $3d^-$  and  $3d^+$ , described in §3. The  $3d^+$  shell is always occupied for the first time at manganese.

It is instructive to compare the steady increase in  $U$  across the series with the more random variations that occur in the band widths of the metals. The d band widths have been calculated by Fletcher and Nudel (1973), and their results have been plotted with the values of  $U$  in figure 4. It is clear that the bandwidth has little correlation with the value of  $U$ . This observation may at first seem only a trivial consequence of the boundary conditions used in our calculation. The boundary conditions (3.3) are correct only for an electron state at the bottom of the band ( $k = 0$ ) and therefore no information about the band structure is carried into the calculation other than the dependence of the band width on  $r_{ws}$ . However, since, in §3,  $U$  was found to vary slowly with the density, and because we believe  $U$  is roughly insensitive to the boundary conditions, it is apparent that it has little dependence at all upon the lattice structure and is nearly wholly a function of the metallic atom's environment alone.

The intrinsic error of our calculation can be taken as the maximum deviation between the various values of  $U$  that could be formed from the eigenvalues in figure 2 and the values that have actually been taken. (It should be stressed that these are systematic errors, principally due to the approximations surrounding equations (2.2) and (2.4). The computations themselves should be correct to many significant figures.) For all materials except chromium the maximum deviation is about 0.3 eV. For chromium only the change in the  $j = l + \frac{1}{2}$  state eigenvalue was used, and the difference between this and the maximum change in the  $j = l - \frac{1}{2}$  state eigenvalue is 0.6 eV. However, although this doubt remains about the magnitude of  $U$  for each metal, there can be little doubt left that  $U$  is a monotonically increasing function of the atomic number  $Z$  for the transition metals. The shape of the lower curve in figure 4 is clearly established.

The classical studies of the Hubbard model relate the magnetic properties of these materials to the ratio of the repulsive electronic energy between two electrons, the electron-electron interaction energy  $U$ , to the kinetic energy of the electrons as measured by the band width  $W$ . It is this ratio,  $U/W$  which should determine the behaviour and it is plotted for the transition metals in figure 5.

To understand the full import of figure 5, it is edifying to compare the values of  $U/W$

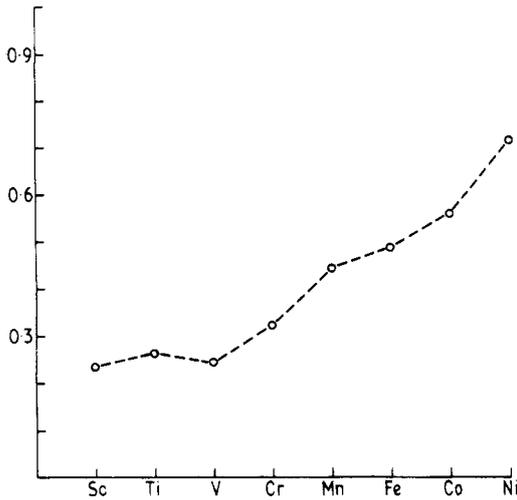


Figure 5. The ratio  $U/W$ .

shown there with the known magnetic properties of the transition metals. The three lowest values of  $U/W$  belong to the metals scandium, titanium and vanadium, all of which are paramagnetic. Cobalt and nickel have the highest  $U/W$  ratios, and each of these metals is ferromagnetic in all phases.

For iron and manganese the experimental observations are more complex. The stable phase of iron at room temperature is fcc and it is ferromagnetic. But iron also possesses a high temperature bcc phase, which, when retained to low temperature, is observed to be antiferromagnetic. Manganese possesses three important phases. Two of these, the complex bcc structured  $\alpha$  phase which is stable at room temperature and a fcc high temperature phase which can be retained at low temperatures, show antiferromagnetic ordering. The third is another high temperature phase, nearly bcc but different in structure to the  $\alpha$  phase, and this is a paramagnetic metal at low temperatures. From figure 5 it can be seen that manganese and iron have middle range values of the ratio  $U/W$ , around 0.45.

From the preceding paragraphs it appears that the critical value of  $U/W$  above which one can expect some type of magnetic ordering is given by

$$U/W \simeq 0.45. \quad (4.1)$$

However, it should be stressed that the considerations above are restricted entirely to localized interactions, and ignore possible band anomalies which themselves may lead to magnetic ordering. For example, in the simple picture presented above, one would expect that chromium, with a ratio  $U/W$  not greatly larger than those of the paramagnets scandium, titanium, and vanadium, might also be paramagnetic. It is in fact antiferromagnetic. However, chromium is a very different type of antiferromagnet to the usual anti-aligned atomic spin situation in that its magnetism is due to a spin density wave whose wavelength is incommensurate with the atomic spacing (Overhauser 1962, Bacon 1961). This has been successfully interpreted by Fedders and Martin (1966), in terms of the special shape of the Fermi surface in chromium. The Fermi surface 'nests' in that there are two regions separated by an almost constant vector  $\mathbf{q}$

in reciprocal space, and it is this vector which determines the wavelength of the spin density wave.

The value of  $U$  which we have calculated is the input value for the Hubbard Hamiltonian. The critical ratio in (4.1) represents the effect of correlation energy on the determination of the magnetism of the ground state. This simple approach has ignored band structure, which may have special features such as that which led to the spin density wave in chromium. However, the balance of importance seems to lean on the side of the atomic environment, rather than band structure. In particular it is interesting to note that where  $U/W$  is large, the magnetic condition of the ground state is experimentally observed to be independent of crystallographic phase: when  $U/W > 0.55$  the materials are ferromagnetic in all their phases. This suggests that if  $U/W$  is large enough the magnetic properties are relatively insensitive to band structure.

### Acknowledgments

The authors are indebted to Dr C F Osborne of the Caulfield Institute of Technology for early discussions on this project and to Drs J H Smith, G C Fletcher and R Street of Monash University for discussions on the interpretation of the results.

### Appendix

In the standard treatments (cf Thouless 1961) a creation operator,  $a_{\alpha}^{+}$ , is associated with a single particle orbital,  $\phi_{\alpha}(\mathbf{r}, \sigma)$  so that the Fock space vector  $|\dots n_{\alpha} \dots\rangle$  has a Slater determinant as its configurational space representation

$$\frac{1}{\sqrt{N!}} \prod_{\alpha} (a_{\alpha}^{+})^{n_{\alpha}} |0\rangle = |\dots n_{\alpha} \dots\rangle \Rightarrow \frac{1}{\sqrt{N!}} \det |\phi_{\alpha}(\mathbf{r}_{\beta}, \sigma_{\beta})|. \quad (\text{A.1})$$

When the overlap between the single particle orbitals is

$$S_{\alpha\beta} = \int \phi_{\alpha}^{*} \phi_{\beta} \, d\tau \quad (\text{A.2})$$

then the creation and destruction operators satisfy the commutation relation

$$[a_{\alpha}, a_{\beta}^{+}]_{+} = S_{\alpha\beta}. \quad (\text{A.3})$$

For orthonormal single particle orbitals this is the usual commutation relation which has been assumed in discussions of the Hubbard model. This is not the meaning of these operators in the present paper.

The Fock space representation does not have to be related to the configurational space representation by means of equation (A.1). Whenever there is a one to one correspondence between a many particle function  $\psi \dots n_{\alpha} \dots (\mathbf{r}_1, \sigma_1; \dots)$  and a set of 'occupation' numbers,  $\dots n_{\alpha} \dots$ , then the Fock space vector may be defined as having the configurational representation

$$|\dots n_{\alpha} \dots\rangle \Rightarrow \psi \dots n_{\alpha} \dots (\mathbf{r}_1, \sigma_1; \dots) \quad (\text{A.4})$$

instead of equation (A.1). Correspondences of this form occur quite often: they occur whenever the interaction between particles may be adiabatically switched on without

degeneracies occurring. A correspondence of this type certainly exists with the different selfconsistent configurations used in the present paper.

The creation and destruction operators may be defined such that

$$a_{\alpha} |n_1, n_2 \dots n_{\alpha} \dots\rangle = (-1)^{\sum_{\beta=1}^{\alpha-1} n_{\beta}} n_{\alpha}^{1/2} |n_1 \dots n_{\alpha} - 1 \dots\rangle \quad (\text{A.5})$$

and

$$a_{\alpha}^{+} |n_1, n_2 \dots n_{\alpha} \dots\rangle = (-1)^{\sum_{\beta=1}^{\alpha-1} n_{\beta}} (1 - n_{\alpha})^{1/2} |n_1 \dots n_{\alpha} + 1 \dots\rangle. \quad (\text{A.6})$$

The factors imply an assumption that  $(a_{\alpha})^2 = 0 = (a_{\alpha}^{+})^2$  and the plus-minus factor is defined such that

$$a_{\alpha} a_{\beta} + a_{\beta} a_{\alpha} = 0 \quad (\text{A.7})$$

and

$$a_{\alpha}^{+} a_{\beta}^{+} + a_{\beta}^{+} a_{\alpha}^{+} = 0 \quad (\text{A.8})$$

and

$$a_{\alpha} a_{\beta}^{+} + a_{\beta}^{+} a_{\alpha} = \delta_{\alpha\beta}. \quad (\text{A.9})$$

With this definition the usual transliteration between the operator in configurational space and the Fock space operator cannot be used. But, in principle, the effect of any operator on a Fock space vector may be expressed as a linear combination of such vectors. Equations (A.5), (A.6) then allow the operator to be written in terms of creation and destruction operators.

## References

- Abdulnur S F, Linderberg J, Öhrn U and Thulstrup P W 1972 *Phys. Rev. A* **6** 889–98
- Adler D 1968 *Solid State Physics* vol 21 ed F Seitz, D Turnbull and H Ehrenreich (New York: Academic Press) pp 1–113
- 1970 *Essays in Physics* **1** 33–77
- Bacon G E 1961 *Acta Crystallogr.* **14** 823–9
- Berggren K F 1972 *Phys. Rev. B* **6** 2156–61
- Brooks H 1958 *Nuovo Cim. Suppl.* **7** 165–244
- Chodorow M 1939 *Phys. Rev.* **55** 675
- Conference Report on Hubbard Hamiltonian 1968 *Rev. Mod. Phys.* **40** 790–811
- Coulthard M A 1967 *Proc. Phys. Soc.* **91** 44–9
- 1973 *J. Phys. B: Atom. Molec. Phys.* **6** 2224–35
- Cyrot M 1972a *J. Phys., Paris* **33** 125–34
- 1972b *Phil. Mag.* **25** 1031–9
- Fedders P A and Martin P C 1966 *Phys. Rev.* **143** 245–59
- Fletcher G C and Nudel B A 1973 *Int. J. Quantum Chem. Symp. No. 7*
- Friedel J 1969 *Physics of Metals* ed J M Ziman (Cambridge: Cambridge University Press) pp 340–408
- Grant I P 1970 *Adv. Phys.* **19** 747–811
- Heeger A J 1969 *Solid State Physics* vol 23 ed F Seitz, D Turnbull and H Ehrenreich (New York: Academic Press) pp 303–21
- Herbst J F, Lowy D N and Watson R E 1972 *Phys. Rev. B* **6** 1913–24
- Herring C 1966 *Magnetism* ed G T Rado and H Suhl (Academic Press: New York) pp 187–240
- Hodges L, Watson R E and Ehrenreich H 1972 *Phys. Rev. B* **5** 3953–71
- Hubbard J 1963 *Proc. R. Soc. A* **276** 238–51
- 1964a *Proc. R. Soc. A* **277** 237–59

- 1964b *Proc. R. Soc.* **A281** 401–19  
——— 1965 *Proc. R. Soc.* **A285** 542–60  
——— 1966 *Proc. R. Soc.* **A296** 82–99  
Ikeda M A, Larsen U and Mattuck R D 1972 *Phys. Lett.* **39A** 55–6  
Johansson B 1973 *J. Phys. C: Solid St. Phys.* **6** L71–4  
Mott N F and Zinamon Z 1970 *Rep. Prog. Phys.* **33** 881–940  
Overhauser A W 1962 *Phys. Rev.* **128** 1437–52  
Segall B 1962 *Phys. Rev.* **125** 109–22  
Siegel E J 1973 *Phys. Stat. Solidi* (b) **55** 817–30  
Siegel E J and Kemeny G 1972 *Phys. Stat. Solidi* (b) **50** 593–606  
Thouless D J 1961 *The Quantum Mechanics of Many-Body Systems* (London: Academic Press)  
Tucker T C, Roberts L D, Nestor C W Jnr, Carlson T A and Malik F B 1969 *Phys. Rev.* **178** 998–1008  
Watson R E 1960 *Phys. Rev.* **118** 1036–45  
Wigner E and Seitz F 1933 *Phys. Rev.* **43** 804–10  
Wyckoff R W G 1948 *Crystal Structures* (New York: Interscience)