

Quantum-statistical calculations of atomic energies and further parameters for zero Kelvin temperature

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 5847

(<http://iopscience.iop.org/0953-8984/1/34/003>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.93

The article was downloaded on 10/05/2010 at 18:40

Please note that [terms and conditions apply](#).

Quantum-statistical calculations of atomic energies and further parameters for zero Kelvin temperature

H Szichman† and H Hora‡

† Department of Theoretical Physics, University of New South Wales Kensington, Australia 2033 and Department of Plasma Physics, Soreq Nuclear Research Center, Yavne 70600, Israel

‡ Department of Theoretical Physics, University of New South Wales Kensington, Australia 2033

Received 27 January 1989, in final form 17 March 1989

Abstract. The quantum-statistical model (QSM) is studied by calculating various atomic parameters near the normal state and beyond it. It is shown from the results of this work that the strength parameter controlling the Kirzhnits–Weizsäcker gradient term is equal to $\frac{1}{2}$ only for extremely high atomic electron densities exceeding 60 \AA^{-3} . Below this limit, due to the variational principle, this parameter may acquire other values. It is shown, by means of a semi-empirical approach, that a value of $\frac{1}{2}$ for this parameter provides calculated atomic binding energies as close as 0.5% of the experimental ones for the first 28 elements. At the same time the classical Weizsäcker value of unity was found not to be able to reproduce accurately any useful property of solid matter. A numerical procedure is also presented for the calculation of the equation-of-state (EOS) at zero temperature which may be easily generalised to give all the finite temperature effects accurately.

1. Introduction

For the past several decades there has been considerable discussion in the physics community as to whether the statistical Thomas–Fermi (TF) [1, 2] and Thomas–Fermi–Dirac (TFD) [3] models, including gradient terms of the Weizsäcker type [4], are able to reproduce important atomic parameters accurately, notably the atomic binding energy, by describing the many-particle system solely by means of the electron density and without making any reference to individual electron wavefunctions [5–8]. This debate was motivated mainly by the widespread use of these models in various fields of physics [9–11], because of the simplicity of their formulation which is to some extent in contrast to the situation of the detailed configuration-type theories.

The gradient correction to the statistical kinetic energy is written in the following form:

$$E_w = \int \frac{\sigma}{8} \times \frac{\hbar^2}{m} \left(\frac{\nabla n}{n} \right)^2 n(r) d^3r \quad (1)$$

where $n(r)$ is the inhomogeneous electron density inside the atom. Von Weizsäcker [4], who first suggested the addition of this term, performed the calculation of the binding energies for the triad of elements O, Mo and Hg making the explicit choice of σ equal to unity. The results obtained were more than 3% above the experimental values, which

at that time was taken to be a great success considering the poor accuracy with which the experimental results were then known. However, as more accurate values became available [12] the discrepancies were seen to be more evident. A further difficulty to this theory became evident when perturbation theories [13–15] showed in different ways that the expansion of the Hamiltonian operator in powers of \hbar leads to a second order gradient correction of the type of equation (1) where σ was predicted to be nine times smaller than Weizsäcker's original value. Those who criticised this last approach could argue then [5, 7] that being (1) a positive correction to a negative binding energy quantity, Weizsäcker's value of σ could therefore give an upper bound to the exact energy and consequently a lower value of this parameter would not be able to improve the agreement with experiment. As a matter of fact, one has to view these earlier computations of binding energies based on equation (1) with a certain degree of caution. The most interesting feature of introducing the correction (1) to the Hamiltonian operator is given by the fact that it produces a finite electron density near the nucleus [16], but it is quite uncertain whether this condition prevailed in the above mentioned calculations. In addition, equation (1) becomes divergent near the nucleus and it is therefore necessary to adopt ad-hoc procedures in order to provide a finite result [17].

A sounder approach to the solution of this problem was first proposed by Kalitkin and Kuz'mina [18] in 1972 and it took the form of resolving directly the fourth order differential energy equation (even though not in its complete form) by means of numerical methods. They called their method the quantum statistical model (QSM). Later on, More [19] gave a more theoretical foundation to his model and Perrot [20] studied approximate solutions to the generalised finite temperature equations. Very recently new research has been published [21, 22], treating some relevant topics connected with the Weizsäcker correction though not using the QSM formalism. However, in our opinion the question posed at the beginning of this paper has not been adequately answered to date. Since it has recently [23] been shown that the TFD solutions can be reduced from their second order form to an iterative single integral representation with a straightforward numerical solution, a legitimate question then arises: what is the use of significantly increasing the computation time with more complex equations if the changes in the results are not significant when compared for example, with fluctuations caused by the shell structure effects? It is also still not clear to what extent this model is valid as well as the exact nature of the strength parameter σ in equation (1).

In this paper we re-examine the correctness of the QSM formalism by calculating diverse atomic parameters for a large number of elements over a wide range of matter densities (we have limited ourselves to the case of zero temperature) and compare them either with experimental values or with results obtained from other theories.

Our work differs from similar studies on this subject [21, 24] in the fact that the QSM offers a more consistent way of calculating atomic binding energies and it likewise differs from Refs. 10 and 25 because we are able to build up EOS tables as well. Finally when comparing our calculations with augmented plane wave (APW) band-structure computational results found in the SESAME EOS-tables [26] or with results from the augmented spherical wave (ASW) method [22], we did that by stressing the average behaviour of the atom pressure rather than the detailed comparison the electron density at the nucleus as reported by More [19].

2. The theoretical model

2.1. Basic equations

The addition of the von Weizsäcker inhomogeneity (1) to the energy equation, within

the ion-sphere model (ISM) [1] at the absolute zero temperature, leads to the following differential equation for the electron density $n(r)$:

$$\frac{\hbar^2}{2m} (2\pi^2 n)^{2/3} - \frac{e^2}{\pi} (3\pi^2 n)^{1/3} + \frac{\sigma}{8} \times \frac{\hbar^2}{m} \left[\left(\frac{\nabla n}{n} \right)^2 (1 - \gamma) - \frac{2\nabla^2 n}{n} \right] + eV(r) = 0 \quad (2)$$

where $V(r)$ is the self consistent solution of the Poisson equation

$$\nabla^2 V(r) = -4\pi en \quad (3)$$

Equation (2) differs from a similar expression given in Ref. 19, by the factor

$$\gamma = \frac{\partial \ln \sigma}{\partial \ln n} \quad (4)$$

which takes into account the dependence of σ on the electron density $n(r)$ (or atomic radius).

As was mentioned in the introduction, equation (2) may be obtained from perturbation theories in which case $\sigma = \frac{1}{8}$ and $\gamma = 0$, but it is also deducible from variational principles by minimising the free energy density $F[n(r)]$, as developed by Kohn and Sham [19, 27]. This formalism is used to calculate $n(r)$ in the following way.

The free energy density is decomposed into the four terms

$$F[n(r)] = F_k + F_r + F_x + F_w \quad (5)$$

where F_k represents the kinetic contributions, F_r is the potential energy which accounts for the electron–nucleus and electron–electron interaction, F_x is the electron exchange free energy and F_w is the gradient contribution [see equation (1)]. The expressions corresponding to these four terms [27, 4] are:

$$F_k = \frac{3}{10} \frac{\hbar^2}{m} (3\pi^2 n)^{2/3} n \quad (6)$$

$$F_r = eV(r)n \quad (7)$$

$$F_x = -\frac{3e^2}{4\pi} [3\pi^2 n]^{1/3} n \quad (8)$$

$$F_w = \frac{\sigma \hbar^2}{8 m} \left(\frac{\nabla n}{n} \right)^2 n \quad (9)$$

The minimisation of F ,

$$\delta F[n(r)] / \delta n(r) = 0 \quad (10)$$

is carried out using equation (6–10) resulting in equation (1).

The variational method is unaffected by the nature of the gradient parameter σ . It is customary to adopt a constant value for this parameter ($\gamma = 0$), but numerical results presented and in this paper show that it in fact represents a limiting value corresponding to a certain configuration of the atom. Even though the determination of the value $\frac{1}{8}$ for σ , as given by the perturbation theories, may be questionable one conclusion of these models [14] is worth taken into account when trying to fit σ to results of detailed configuration models. It is that the gradient expansion gives only a limited representation of the atom state since it avoids the singularities of the electronic polarisability as expressed in the random phase approximation (RPA) [15] theory.

2.2. Self consistent solutions of the Poisson equation and boundary conditions

Equation (2) is a fourth order differential equation requiring four boundary conditions to be solved uniquely. Two of these boundary conditions are provided by the ISM

configuration. In this model the nucleus together with Z electrons are confined in an ion sphere having a radius r_0 such that

$$r \leq r_0 = (\frac{3}{4\pi} n_1)^{1/3} \quad (11)$$

Where n_1 is the total ion density. The first boundary condition is given by the conservation of particles within the ion sphere, i.e.,

$$Z = \int_0^{r_0} n(r) d^3r \quad (12)$$

We also require the central potential $V(r)$ inside the atom to have a Coulomb like character near the nucleus, so that

$$rV(r)|_{r=0} = -Ze \quad (13)$$

Under the conditions dictated by equations (12) and (13), the self-consistent solution of the Poisson equation (3) in the ISM is given by [2]

$$-eV(r) = \mu + \frac{4\pi e^2}{r} \int_0^{r_0} n(r')(r' - r)r' dr' \quad (14)$$

where μ is the chemical potential which is determined in such a manner that equation (12) is observed. Direct differentiation of equation (14) yields

$$\frac{\delta V(r)}{\delta n(r)} = 0 \quad (15)$$

$$\varepsilon_r = -\frac{\delta V(r)}{\delta r} = \frac{e}{r^2} \int_r^{r_0} n(r') d^3r' \quad (16)$$

i.e., the potential $V(r)$ at r becomes an extremum as a function of the electron density and the electron field inside the ion at a distance r of the nucleus is the same as that produced by a point charge at the nucleus and equivalent to the charge between the distance r and infinity thus assuring the neutrality of the atom in the space outside the ion-sphere. It is instructive to point out that conditions (15) and (16) are generally quoted in the literature as complementary requisites of the ISM, but the present analysis shows that they are a direct consequence of the assumption of a spherical symmetrical Coulomb field near the nucleus and the confinement of the atom charge within the limits of the ion-sphere.

In the TF and TFD models (when $\sigma = 0$) the vanishing of the electrical field at the boundaries of the atom is equivalent, in virtue of equation (2), to

$$\left. \frac{\partial n}{\partial r} \right|_{r=r_0} = 0 \quad (17)$$

This boundary condition is also extended to the QSM [18] in order to provide a smooth transition between this last model and the TFD theory as σ approaches zero.

Finally the fourth and last boundary condition is related to the already mentioned are requisite that the QSM electron density should be finite near the nucleus. Expanding the Laplacian and gradient terms of equation (2) in spherically symmetric coordinates, by taking into account equation (13), this condition is expressed by

$$\left. \frac{\partial n / \partial r}{n} \right|_{r=0} = -2Z / \sigma a_0 \quad (18)$$

where $a_0 = \hbar^2 / me^2$ is the Bohr radius. This condition may also be written in a more

convenient form for the present exposition in the following manner. Equation (13) ascribes a Coulomb like nature to the potential near the nucleus. Under such conditions the electron density varies as given by the TF and TFD theories, i.e.,

$$n_{TF}(r) \approx n_{TFD}(r) \propto r^{-3/2} \quad \text{as } r \rightarrow 0$$

Obviously it follows, that a necessary condition to obtain a finite electron density at the centre of the atom in the QSM configuration is then given by

$$r^{3/2} n_{QSM}|_{r=0} = 0 \tag{19}$$

Equation (18) is suitable to obtain a finite electron density at the nucleus by means of analytical methods, but for use in numerical procedures for the simultaneous solution of equation (2) and (14), as explained in Section 3, it is more convenient to use equation (19) for the fourth boundary condition.

2.3. EQS and the virial theorem in QSM

We may build-up relations between the atomic pressure, energy and volume, i.e., EOS by means of the free energy density F as given by equations (5) to (9), using well known thermodynamic relations. Thus for the pressure we have [3]

$$P = - \left(\frac{\partial A}{\partial V} \right)_{T,Z} \tag{20}$$

where A is the Helmholtz free energy of the atom, the partial differentiation being carried out at constant temperature T and particle number Z . Since we are assuming $T = \text{constant}$ the first condition is fulfilled automatically and as for the second, in the ISM it means that the differentiation should be done at the surface of the atom sphere. This last condition is a clear consequence of the conservations of particles within the ion-sphere [equation (12)]. In addition, in the ISM the electron gas is uniformly distributed along the atom boundaries and the pressure anywhere there will be the same as that exerted by a single electron. The Helmholtz free energy for a single electron is F/n and it occupies a volume of $1/n$.

It follows then, that in terms of the electron density at the atom boundaries, the pressure is given by

$$P = n^2 \left. \frac{\partial}{\partial n} \left(\frac{F}{n} \right) \right|_{r=r_0, T} \tag{21}$$

As we have not thus far made any explicit assumption as to the values of T , this formula is of general application in the ISM configuration. Use of equation (21), taking into account the boundary conditions given by equations (15) and (17), results in

$$P = \frac{1}{5} \left(\frac{\hbar^2}{m} \right) [3\pi^2 n(r_0)]^{2/3} n(r_0) - \frac{e^2}{4\pi} [3\pi^2 n(r_0)]^{1/3} n(r_0) - \frac{1}{4} \sigma \left(\frac{\hbar^2}{m} \right) \nabla^2 n(r_0) \tag{22}$$

The energy E , for the case $T = 0$, is given simply by

$$E = E_k + E_r + E_x + E_w = \int_0^{r_0} F d^3r \tag{23}$$

where each term on the right side of equation (23) represents the contribution of the volumetric integrals of the respective free energy densities given by equation (6) to equation (9).

There is an alternative way of expressing the total energy E by means of the virial theorem which has been shown to hold for the generalised TF atom [1, 2]. In the case of the QSM, it adopts the form [19, 20]

$$3PV = 2(E_k + E_w) + E_r + E_x + E_c \quad (24)$$

where $V = \frac{4}{3}\pi r_0^3$ is the atomic volume and E_c is given by [19].

$$E_c = -\frac{3}{4} \frac{\hbar^2}{m} \int_0^{r_0} \sigma \nabla^2 n \, d^3r \quad (25)$$

For constant σ , this expression becomes a surface integral by virtue of Gauss' theorem and its value vanishes because of boundary condition (17), but in the general case should be taken into account. It follows then that E is also given by

$$E = (3PV + E_r + E_x - E_c)/2 \quad (26)$$

$$= 3PV - (E_k + E_w + E_c) \quad (27)$$

The differences between the values calculated for E by means of equations (23), (26) and (27) will give an idea of the accuracy of the numerical procedure applied in solving the basic equations of Sections 2.1 and the correctness of the results obtained. It can incidently be observed that equation (26) is also the average value among all these expressions for the atomic energy, and because of that it was adopted for our calculations as the representative value of the binding energy of the atom in agreement with earlier procedures [3].

3. Numerical procedure

A numerical integration procedure, similar to the one described in Ref. 23, was used to integrate equation (13). In this reference, it was pointed out that the zero order solution of equation (2), i.e., the TF and TFD approximations, were obtained in a straightforward and compact way, by an iterative integration of equation (13) from the outer surface of the atom in towards the nucleus. The advantage of such a method is that the temperature effects introduced by the Thomas–Fermi distributions [23] are fully taken into account instead of carrying out approximate interpolations and fitting of analytical functions as done elsewhere [3, 20].

In the TF and TFD models, once given the volume and temperature, the chemical potential μ is determined self-consistently with equation (11). In the QSM we must add two more conditions at the ion-surface, i.e., $n'(r_0)$ and $n''(r_0)$. The first one is zero because of the boundary condition in equation (17) and the last one is determined in such a way that a finite electron density at the nucleus is obtained by means of equation (19). This is performed in the following way: Once given μ and $n''(r_0)$, the electron density at the atom boundaries $n(r_0)$ is obtained as a linear solution of equation (2). Then it follows that

$$n'(r) = - \int_0^{r_0} n''(r) \, dr \quad (28)$$

and

$$n(r) = n(r_0) - \int_r^{r_0} n'(r) \, dr \quad (29)$$

The quantity $n''(r)$ at an interior layer of the atom is fixed in such a way that after being numerically integrated twice, equation (29) gives the same value, within a certain degree of accuracy, as that of the local solution of $n(r)$ by equation (2). This procedure is then followed up to the centre of the atom. The correctness of the results obtained by our method is examined according to the spread of the values calculated for the energy by means of the virial theorem (see § 2.3) and the accuracy to which the neutrality condition (equation (12)) is approached. For the elements studies here, we have inferred an error in the determination of binding energies of less than 0.5% based on the error given by the virial theorem.

4. Results

In order to verify the validity of our representation of the QSM and the method of solving its equations, as described in § 2 and § 3, we calculated several physical parameters such as the atomic binding energies, the pressure of ionisation of the atom, specific volumes and cold pressure curves.

In doing so we have adopted a 'semi-empirical approach', i.e., we have assigned different values to σ (then $\gamma = E_c = 0$, see equations (4) and (25)) and analysed their effect on the computed parameters when compared with experiments or other theoretical estimate. The values of σ chosen were zero (the TF and TFD theories), one and $\frac{1}{8}$, as given by the classical Weizsäcker (indicated henceforth as TFDW) and the expansion theories (QSM). A new value of $\frac{1}{8}$ (indicated throughout the paper as present results) was also used and this gave the best fit to the experimental atomic binding energies.

4.1. Computation of atomic binding energies

In table 1, we summarise the calculations of the atomic binding energy for the first 28 elements, the experimental values for this parameter may be deduced from published data on ionisation potentials [28, 29]. Our computations of the atomic binding energies were done by looking for the minimum of equation (26) as a function of volume. The values obtained with $\sigma = \frac{1}{8}$ (present results) show very good agreement with the experimental values (to better than 0.5%) and approach them more closely than those values given by Barnes *et al* [24] using their so-called quantum and correlation corrected Thomas–Fermi–Dirac (QCCTFD) equations and even more closely than the results obtained with the shell effect oriented non-relativistic Hartree–Fock–Slater (NR-HFS) [30] computations. The computations with $\sigma = \frac{1}{8}$, indicated as QSM, show them to be 4–9% higher than the experimental values for the range of Z up to 28 while $\sigma = 1$ gives an excessively low estimation. We do not as yet have a theoretical justification for the values of $\sigma = \frac{1}{8}$, but the agreement observed here with experiment may be significant and should be taken into account in further investigations with this model.

4.2. The pressure ionisation of the atom

The degree of ionisation of the atom is given by the average number of free electrons moving within the limits of the atom and having a positive energy state that permits them to escape the effects of the central potential. In the average ionisation atom models using the Saha rate equations [31], this phenomenon is mainly attributed to thermal excitations of the atom though it is generally accepted that at increasing densities the atomic states

Table 1. Comparison of binding energies values (eV/atom).

Z	TF	TFD	QSM	TFDW	Present results	QCCTFD ^a	NR-HFS ^b	Expt. ^c
1	20.91880	28.0775	17.996		16.098			13.598
2	105.4241	126.769	86.223		78.464	80.497	78.31327	79.00 [?]
3	271.5311	312.407	221.92		202.85	206.82	196.6371	203.481
4	531.3043	596.355	432.10		400.79	406.65	387.9084	399.139
5	894.2659	987.705	729.97		681.48	688.97	655.2258	670.967
6	1368.431	1494.17	1121.7		1049.6	1061.1	1008.971	1030.08
7	1960.795	2122.50	1651.1		1512.6	1530.0	1458.183	1486.029
8	2677.606	2878.78	2214.2		2075.1	2101.2	2011.968	2043.794
9	3524.541	3768.52	2920.8		2754.8		2679.202	2715.795
10	4506.818	4796.81	3747.8		3543.8	3573.2	3468.920	3511.547
11	5629.281	5968.39	4703.0		4444.7		4369.695	4419.785
12	6896.461	7287.69	5773.6		5469.2		5392.822	5450.559
13	8312.618	8758.88	6968.4	4349	6618.0		6538.176	6604.364
14	9881.785	10385.9	8319.3	5077	7892.2		7811.462	7887.513
15	11607.79	12172.6	9790.5	6024	9315.5		9216.967	9304.609
16	13494.29	14122.4	11404	7067	10847		10759.10	10858.034
17	15544.77	16238.9	13159	8220	12536		12441.89	12554.488
18	17762.57	18525.3	15069	9504	14387		14269.89	14397.512
19	20150.92	22604.3	17124	10904	16366		16233.67	16379.956
20	22712.94	23620.5	19361	12432	18495	18623.0	18341.09	18506.545
21	25451.60	26435.2	21724	14096	20784		20594.90	20782.352
22	28369.80	29432.0	24356	15829	23203		23002.31	23215.894
23	31470.35	32613.4	26954	17737	25825		25568.29	25815.084
24	34755.98	35982.3	29756	19729	28549		28295.14	28586.426
25	38229.33	39541.2	32792	21864	31481		31187.99	31516.672
26	41892.97	43292.7	35991	24148	34563		34249.67	34628.701
27	45749.41	47239.3	39314	26566	37835		37484.03	37931.15
28	49801.08	51383.3	42924	29111	41229		40895.67	41389.273

^a Reference 24.^b Reference 30.^c Reference 28, 29.

are shifted into the continuum resulting in the so-called pressure ionisation of the atomic shells [32]. The exact evaluation of pressure ionisation is a subject of controversy [33] and it is mainly described by phenomenological formulas. The TF model in its different versions has nevertheless the rare feature of being able to give a quantitative estimation of the degree of ionisation of the atom by counting the number of electrons in the atom having a positive energy exceeding the value of the chemical potential on the atom boundaries [23]. This feature can be expressed for the generalised temperature case [23], which for $T = 0$ becomes:

$$Z^* = \int_0^{r_0} \left[n(r) - \left(n(r)^{2/3} - \frac{2}{(3\pi^2)^{2/3}} \frac{\mu}{e^2 a_0} \right)^{3/2} \right] d^3 r, \quad (30)$$

the integration being performed over layers where the integrand gives a real positive number.

As a first consequence of the correlation between Z^* and the pressure exerted on the atom, one would expect that up to the normal state, where $P < 0$, Z^* should be zero. The calculations of equation (30) carried out with the TF and TFD models [23] showed that these approximations do not produce the above mentioned effect, even though the TFD model by itself introduces a great improvement in this respect over previous

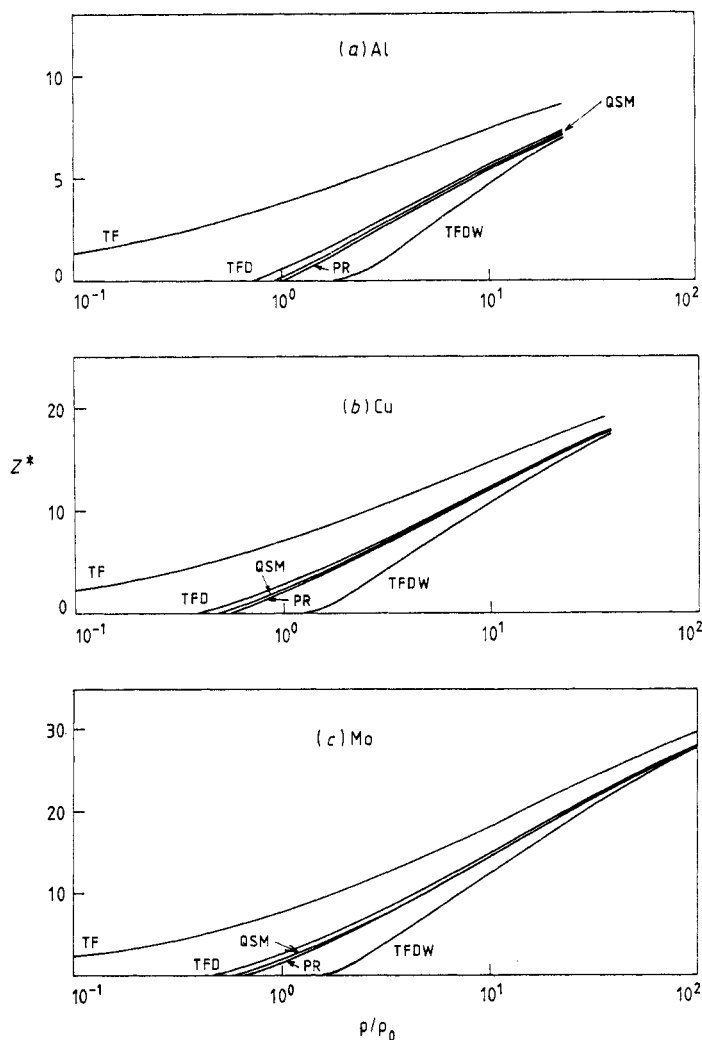


Figure 1. Comparison of the cold pressure degree of ionisation of the atom as a function of the compression according to the different versions of the TF models used in this work for the elements (a) aluminum, (b) copper and (c) molybdenum. (PR: present results).

methods. It is then of interest to elucidate the effect that the QSM introduces in the curves of the pressure ionisation. For that purpose we have calculated the average number of free electrons for a wide range of compressions for the elements aluminum, copper and molybdenum and the results are shown in figures 1(a), 1(b) and 1(c). The use of $\sigma = \frac{1}{2}$ did not produce a zero degree of ionisation at the normal state for any of the cases studied here, while the choice of $\sigma = \frac{1}{3}$ only produced such effect in aluminum. Neither parameter gives satisfactory results indicating that, unlike the case of the atomic binding energy, the shell effect has more influence in the determination of the pressure ionisation of the atom, at least near the crystal state.

We observe nevertheless that the value of $\sigma = 1$ does provide the feature of a vanishing Z^* for the normal state for each one of the elements studied in figure 1. We consider this fact as rather circumstantial, taking into account the remaining results presented in this paper for such a value. However, it does show how sensitively the determination of the degree of ionisation of the atom depends on the device of σ .

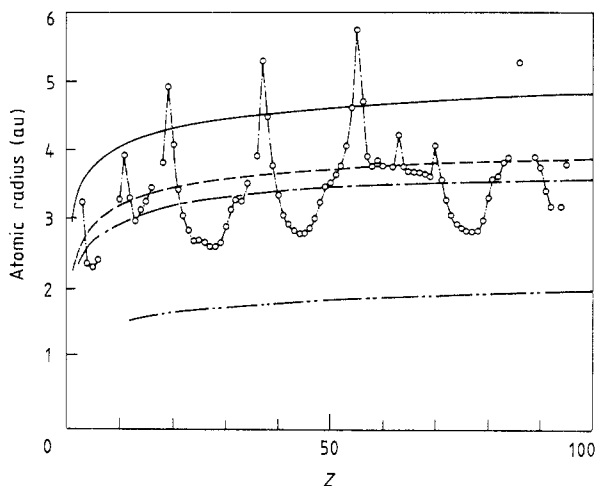


Figure 2. Atomic radii of the elements as a function of atomic number Z compared with computed statistical averages. Experimental values are indicated by open circles; —, TFD results; ---, QSM; - · - ·, TFDW results; —, present results.

4.3. Determination of atomic radii

The atomic volume at which the atom reaches the minimum internal energy, or zero pressure also determines the radius of the normal volume, a figure than can be easily compared with experiment. In figure 2 are shown the experimental atomic radii as a function of Z and they are compared with computed values given by the TFD theory, QSM, TFDW and present results. All these calculations are based on different values of σ whose effect is to lower the TFD curve to give better agreement with the experimental values.

It is quite difficult based on the computations of figure 2, to decide which of the two values of $\frac{1}{9}$ or $\frac{1}{6}$, gives the best result, though a meticulous square fit test would indicate some preference for $\frac{1}{6}$. However, it can be stated beyond any doubt that neither the TFD nor TFDW calculations give a satisfactory result, especially the last one which falls completely out of range of the experimental results.

4.4. Electron pressures and the strength of the gradient contribution

The experimental and computational evidence brought so far does not show that the value of $\sigma = \frac{1}{9}$ has any special meaning for the properties of matter near the normal state, where the QSM is believed to manifest its greater effect. The fact that perturbation theories so consistently predict this value merits some meditation. The common feature of these models is the derivation of the correlation (gradient) effects as a component of the exchange potential added to the central potential of a uniform non-interacting electron gas. The correct functional dependence of the exchange operator leads to the assignment of $\frac{1}{9}$ for σ . In addition, if the unperturbed electron gas is restricted to move within the limits of the atomic volume, the solution will be self-consistent only if all the terms arising from the gradient expansions are taken into account [15]. The QSM resolves the atom equations in a quite different way. The series are truncated at the gradient correction, when this last and the exchange term are assumed not to be correlated and the equations are then solved self-consistently by producing a finite electron density at

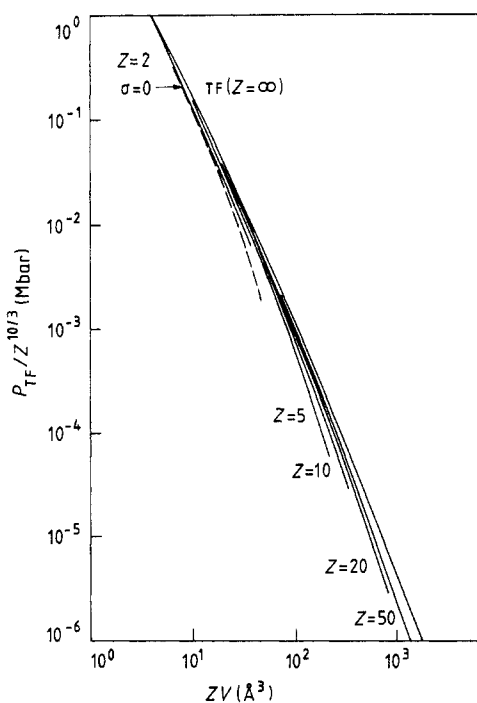


Figure 3. Kinetic pressures according to the TF and QSM theories for different values of Z ; the broken curve indicates a kinetic pressure curve calculated for $Z = 2$ with the TFD model ($\sigma = 0$).

the nucleus. By this procedure the unperturbed density solution ceases to be self-consistent since it is subject to the value of the chemical potential which varies for the same atomic volume according to the statistical model used. It seems obvious that both methods can be correlated only in the high electron density region, when the corrections introduced by the exchange-correlation potential are so small that they cannot appreciably change the distribution of the non-interacting electron gas [15]. A different point of view to that presented in Ref. 7 for the illustration of this fact is shown in figure 3. We have calculated the TF (kinetic) pressure curves by first omitting and then including the exchange-correlation forces for different values of the atomic number Z . The results are shown in figure 3 in TF scaled units in order to facilitate the search for the conditions at which both computations are equivalent. The pressure obtained by the consideration of the exchange-correlation potential was lower than that resulting when they were not taken into account (see figure 3). The difference becomes smaller as the volume decreases or as Z is increased, i.e., the fact that the comparison between the QSM and the perturbation theories is valid at increasing values of the electron density is thus numerically confirmed.

The computations also show that these difference become much smaller as σ is increased. This fact can be intuitively understood, since as the strength of the gradient terms is increased the kinetic energy of the electron gas is also increased (see equation (24)).

The results of figure 3 might suggest that σ acquires its lowest value (believed to be $\frac{1}{2}$) at the border of the atom but it increases near the atom nucleus, as this would improve the agreement between the QSM and the gradient expansion theory. This trend is also

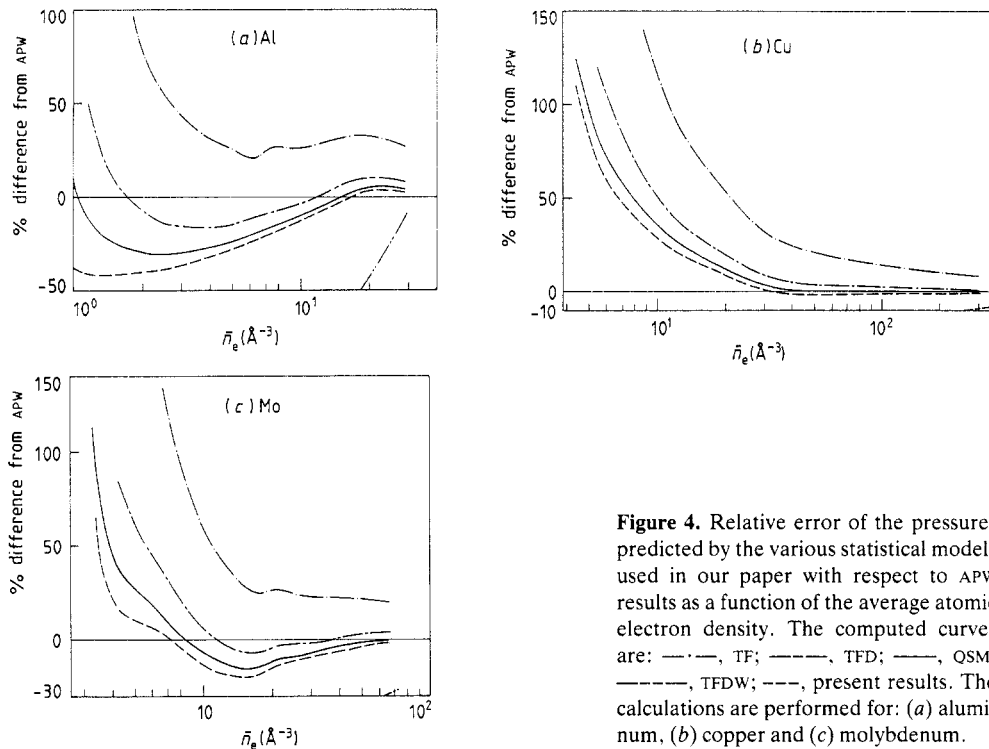


Figure 4. Relative error of the pressures predicted by the various statistical models used in our paper with respect to APW results as a function of the average atomic electron density. The computed curves are: — · —, TF; — — —, TFD; — — —, QSM; — — — —, TFDW; - - - -, present results. The calculations are performed for: (a) aluminum, (b) copper and (c) molybdenum.

confirmed by the results on binding energies, shown in table 1. As can be observed, the tendency of the present theoretical results is to approach the experimental ones from above at low Z , and from below at high values of Z .

Finally, we tried to verify numerically that $\frac{1}{2}$ is indeed the proper value of σ to use at very high compressions. For this purpose we calculated the pressure curves of the elements aluminum, copper and molybdenum and compared them with standard APW computations for the same elements [26]. This model has been shown to give results in excellent agreement with semi-empirical calculations of cold pressure curves [34] and it is believed to provide an accurate standard for the evaluation of statistical models [19]. The results of our studies are shown in figure 4 where the relative departure from the APW values is plotted against the average atomic electron density, which according to what has been mentioned previously, seems to be the most suitable parameter. From figure 4(b) and 4(c) which show the computations carried out for copper and molybdenum respectively, it is clear that the pressures in the limit are best fitted by $\sigma = \frac{1}{2}$, but that occurs only at average electron densities beyond 60\AA^{-3} , where the accuracy of the values given by the QSM is better than 1%. Below the above mentioned threshold little can be said about the improvements of the QSM since the oscillations around the APW values associated with band crossings are so large that they make the differences between the different statistical models meaningless. In the case of aluminum (see figure 4(a)) the data available on APW pressures [26] did not permit a comparison beyond a values of 30\AA^{-3} for the average atomic electron density. Up to that point data presented in figure 4(a) confirmed the trends mentioned above and as for the limiting value of σ , the results reported by More [19] seem to give support to our previous former conclusions concerning the best value for σ .

Another surprising conclusion arising from figure 4, is that even though we have extended our calculations to an extremely high electron density, the inaccuracy of the

TF model is still high (about 17–20% error) and it is unable in this whole range of compressions to approach the average of the oscillations originated in the shell structure effect. Under the same conditions, the TFD model gives an error of only 3% and it is able to take these oscillations into account.

5. Conclusions

The results presented in this paper indicate that the assignment to the gradient parameter of a value of $\frac{1}{5}$ as predicted by the perturbation theories is correct only if all the terms of the gradient expansion are taken into account. The QSM theory in its actual form gives reliable results only at average atomic electron densities above 60 \AA^{-3} , when shell structure effects become negligible. Because of series truncation, the value of σ must change if we want to accurately reproduce atomic volumetric parameters as compressions values are decreased as is shown by the results obtained in this work. In this context, our fitted value of $\sigma = \frac{1}{5}$ is not in contradiction with the value of $\frac{1}{5}$ found by Tomishima *et al* [10] for this same parameter or the value of $1/5.38$ advocated by Lieb [35] on the basis of theoretical considerations, as these authors have performed their calculations for an infinite atomic volume, a fact which further confirms the tendency observed in this work of an increasing value of σ with increasing atomic volumes. Alternatively various authors [7, 10, 19] have expressed the opinion that for a better description of the atom properties at zero temperature by means of the QSM theory, a dependence of σ on the electron density or distance r from the atom nucleus should be considered as has been suggested by us in section 4. The exact formulation of σ as a function of the electron density will not be unique for the reasons mentioned at the beginning of these conclusions, but will depend on the optimisation of the physical atom properties investigated. It would then be of interest to extend the studies performed with the present formulation of the QSM to other atomic parameters near the normal state which are in common use.

The present formulation of the QSM can be easily generalised for the exact computation of all the finite temperature effects [23], thus permitting the rapid approximate computation of EOS and other important properties like, e.g., the polarisation shift of spectral lines in high density plasma [36, 37]. This is still conditional upon a consistent formulation of σ as a function of electron density and temperature and for this task the QSM merits further attention.

Acknowledgments

One of the authors gratefully acknowledges Dr A Krumbein for critical reading of the manuscript. He would also like to thank Professor H Hora for the generous hospitality and cooperation while spending a sabbatical in the UNSW.

This work was supported by the Australian Research Grant Scheme, ARGs, No. 81B/15511.

References

- [1] Feynman R P, Metropolis N and Teller E 1949 *Phys. Rev.* **75** 1561
- [2] Latter R 1955 *Phys. Rev.* **99** 1854; 1956 *J. Chem. Phys.* **24** 280

- [3] Cowan R D and Ashkin J 1957 *Phys. Rev.* **105** 144
- [4] Von Weizsäcker C F 1935 *Z. Phys.* **96** 431
- [5] Gombás P 1969 *Phys. Lett.* **28A** 585
- [6] Schey H M and Schwartz J L 1965 *Phys. Rev.* **137** 709
- [7] Jones W and Young W H 1971 *J. Phys. C: Solid State Phys.* **4** 1322
- [8] Goodisman J 1970 *Phys. Rev. A* **1** 1574
- [9] Golden S 1957 *Phys. Rev.* **105** 604
- [10] Tomishima Y and Yonei K 1966 *J. Phys. Soc. Japan* **21** 142
- [11] Perrot F 1978 *Phys. Status Solidi B* **87** 707
- [12] Moore C E 1952 *Natl. Bur. Std. (US) Circ.* **467**
- [13] Kirzhnits D A 1957 *Sov. Phys.-JETP* **5** 64
- [14] Kompaneets A S and Pavlovskii E S 1957 *Sov. Phys.-JETP* **4** 328
- [15] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** 864
- [16] Steiner E 1963 *J. Chem. Phys.* **39** 2365
- [17] Kalitkin N N 1960 *Sov. Phys.-JETP* **11** 1106
- [18] Kalitkin N N and Kuz'mina L V 1972 *Sov. Phys.-Solid State* **13** 1938
- [19] More R M 1979 *Phys. Rev. A* **19** 1243
- [20] Perrot F 1979 *Phys. Rev. A* **20** 586
- [21] Becke A D 1988 *J. Chem. Phys.* **88** 1059
- [22] Zittel W, Meyer-ter-Vehn J and Kubler J 1987 *Solid State Commun.* **62** 97
- [23] Szichman H, Eliezer S and Salzmänn D 1987 *JQSRT* **38** 281
- [24] Barnes J F and Cowan R D 1963 *Phys. Rev.* **132** 236
Barnes J F 1965 *Phys. Rev.* **140** 721
- [25] Yonei K and Tomishima Y 1965 *J. Phys. Soc. Japan* **20** 1051
- [26] Los Alamos Scientific Laboratory 1978 Report No. LA-7130 unpublished
- [27] Kohn W and Sham L J 1965 *Phys. Rev. A* **140** 1133
- [28] Allen C W 1973 *Astrophysical Quantities* (London: Athlone) p 37–40
- [29] Lang K R 1974 *Astrophysical Formulae* (New York: Springer) p 246–8
- [30] Snow E C, Canfield J M and Waber J T 1964 *Phys. Rev.* **135** A969
- [31] Griem H 1964 *Plasma Spectroscopy* (New York: McGraw-Hill)
- [32] Salzmänn D and Krumbein A 1978 *J. Appl. Phys.* **49** 3229
- [33] More R M 1983 *Atomic and Molecular Physics of Controlled Thermonuclear Fusion* ed. C J Joachain and D E Post (New York: Plenum) p 399–440
- [34] Szichman H and Krumbein A D 1986 *Phys. Rev. A* **33** 706
- [35] Lieb E H 1981 *Rev. Mod. Phys.* **53** 603
- [36] Henry B I and Hora H 1983 *Opt. Comm.* **44** 185
- [37] Salzmänn D and Szichman H 1987 *Phys. Rev. A* **35** 807