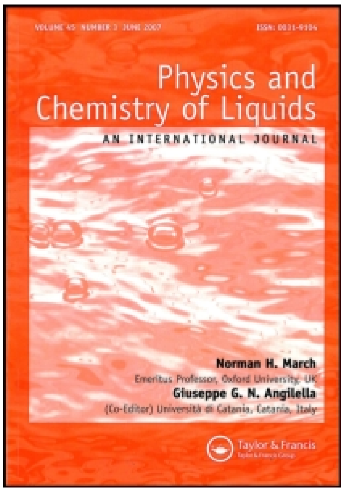

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SOFT CORE DESCRIPTION OF THE STRUCTURE OF LIQUID RARE EARTH METALS

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We present the results of analysis of the observed structure factors $S(k)$ of liquid 4f rare earth metals. We have assumed a repulsive Yukawa potential as a convenient choice of reference potential, and have carried out the calculations within the mean spherical approximation (MSA). Our analysis only gives qualified support to the view that there is a hardening of the cores as the 4f-band is filled across the lanthanides for La to Lu.

KEY WORDS: 4f rare earths, Yukawa potential, mean spherical approximation.

1 INTRODUCTION

In a recent paper[1] we used a repulsive Yukawa potential to interpret the observed structure factors $S(k)$, near melting, of the liquid 3d transition metals at large momentum transfer, as this region is expected to be determined primarily by the repulsive core of the effective interionic potential. The results obtained supported the view, originally put forward by Waseda and Tamaki[2], that $S(k)$ exhibits a trend towards the hardening of the cores as the 3d-band is filled. However, this trend is not as straightforward as implied by the more qualitative hard-sphere analysis of Ref. 2, and our work indicates that there are subtler energy contributions which cannot be ignored in the middle of the 3d series.

In this note we complete our calculations with a similar analysis of the liquid 4f rare earth metals. Experimental information of $S(k)$ for these melts is available from both X-ray[3,4] and neutron data[5,6,7] covering most of the elements in the series with the exceptions of Pm, Sm and Tm. However, in our analysis we shall be using the complication of X-ray data as presented in Waseda's book.[8] It has been suggested by

Waseda[9], in a hard sphere analysis of the experimental data that, similarly to the liquid 3d transition metals, there is a hardening of the cores as the 4f-band is filled across the lanthanide series from La to Lu. We shall be examining this assertion when, in Section 3, we discuss the results of this work. In Section 2 we describe briefly the elements of the theory used in this work.

2 THEORY

As stated earlier we shall be using a potential of the type

$$\beta v(r) = \begin{cases} \gamma \exp(-k_s x)/x & x > 1 \\ \infty & x < 1 \end{cases} \tag{2.1}$$

to interpret the observed $S(k)$, near melting, of the lanthanide series. In Eq. (2.1), $\beta \equiv (k_B T)^{-1}$, where T is the temperature and k_B the Boltzmann constant; and $x = r/\sigma$, with σ denoting a hard core diameter. γ and k_s are taken as two adjustable parameters which may be loosely identified with the strength and softness of the potential, respectively.

To calculate $S(k)$ we use the Yukawa potential given above, together with the Mean Spherical Approximation (MSA) of liquids which is defined by the Ornstein–Zernike equation

$$h(r) = c(r) + n \int dr' c(r') h(|r - r'|) \tag{2.2}$$

together with the closure

$$h(r) = -1 \qquad \text{for } r < \sigma \tag{2.3}$$

$$c(r) = -\beta c(r) \beta v(r) \qquad \text{for } r > \sigma \tag{2.4}$$

In Eqs. (2.2) to (2.4) $h(r) = g(r) - 1$, and is the total correlation function, $g(r)$ is the pair distribution function, while $c(r)$ denotes the direct correlation function and n is the number density. Equation (2.3) is an exact result reflecting the presence of the hard core at $r = \sigma$; whereas (2.4) is an approximation assuming that the asymptotic behaviour of $c(r)$ holds for all values of r beyond the hard core.

Fourier transforming (2.2), it is possible to define the following relationship between $S(k)$ and $\tilde{h}(k)$, or $\tilde{c}(k)$,

$$S(k) \equiv 1 + n\tilde{h}(k) \tag{2.5}$$

$$= [1 - n\tilde{c}(k)]^{-1} \tag{2.6}$$

with the Fourier transform of the correlation functions given by

$$\tilde{f}(k) = \int dr f(r) e^{ik \cdot r} \tag{2.7}$$

The advantage of using the MSA for the Yukuwa potential is that an analytic solution is available, leading to a closed analytic form for $S(k)$[10], which we use in this work. This was originally used by Hayter *et al.*[11] to describe $S(k)$ for the liquid alkali metals very accurately.

Following previous work[1,12] we have matched the MSA $S(k)$ of the potential given by Eq. (2.1) to obtain the set of parameters γ, k_s and σ which best reproduce the experimental structure factors of the liquid 4f rare earth metals. In practice we chose γ, k_s and σ so as to minimize

$$\int_{k_1}^{k_5} [S_{\mathrm{exp}}(k) - S(k)]^2 k^2 dk \qquad (2.8)$$

where k_1 and k_5 correspond to the first and fifth nodes beyond the principal peak.

3 RESULTS AND DISCUSSION

By the above method we establish the data of Table 1 and these are the basis of all our subsequent discussion. In all cases the input data are the temperature T and the number density n.

We first note that, as in our WCA analysis[12], Table 1 shows that at melting the lanthanides have the smallest packing fractions of all the systems we studied (alkalis, transition and rare earth metals). The use of the term 'packing fraction' is appropriate only for hard sphere systems. We use the term somewhat loosely in the present case. It is also worth noting that the values obtained for the hard sphere diameters are smaller than those obtained using both the WCA procedure[12] and the HS results of Waseda[8] (see also Harder and Young[13]). Actually the HS cores are bracketed, in this case, between the MSA and WCA values, as shown in Table 2. Since, as already indicated, our WCA model probes the repulsive core at essentially $k_B T$, the Waseda hard sphere model at $3\,k_B T/2$ and the present (MSA) model at various values from $4.5\,k_B T$ to $20.1\,k_B T$, it is to be expected that the hard sphere diameters obtained in each case are

Table 1 Analysis of observed structure factors, data summary. The input data and observed structure factors are taken from Waseda[8].

Rare Earth Metals	*Input*		*Output*				
	T/K	$n/\text{Å}^{-3}$	η	$\sigma/\text{Å}$	k_s	γ	$\beta v(\sigma)$
La	1243	0.0258	0.3114	2.8461	2.59	220	16.60
Ce	1143	0.0287	0.3077	2.7358	2.55	209	16.33
Pr	1223	0.0283	0.3239	2.7960	2.69	233	15.77
Nd	1323	0.0289	0.3360	2.8107	3.64	440	11.52
Eu	1103	0.0183	0.3067	3.1750	5.97	1759	4.49
Gd	1603	0.0265	0.3456	2.9203	2.90	317	17.42
Tb	1653	0.0274	0.3406	2.8742	2.88	340	19.11
Dy	1703	0.0301	0.3487	2.8074	2.98	397	20.10
Ho	1753	0.0301	0.3566	2.8283	5.01	675	4.50
Er	1793	0.0302	0.3595	2.8328	4.45	384	4.50
Yb	1123	0.0216	0.2925	2.9573	5.28	2475	12.59
Lu	1953	0.0316	0.3735	2.8263	3.27	119	4.50

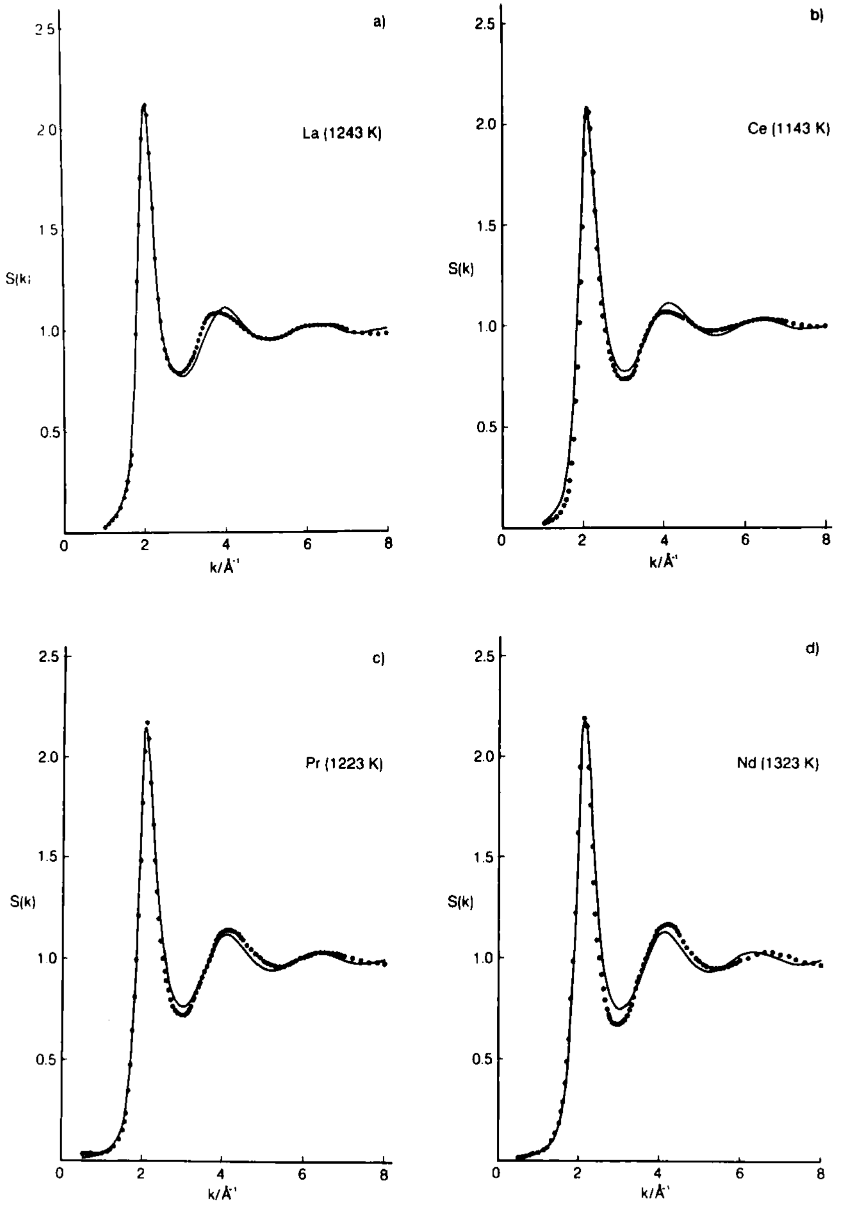

Figure 1 Structure factors of the liquid 4f rare earth metals near melting. Input data, as shown in Table 1, and experimental data, indicated by dots, are taken from Waseda's book[8]. The continuous lines refer to theory (this work). a) La; b) Ce; c) Dr; d) Nd.

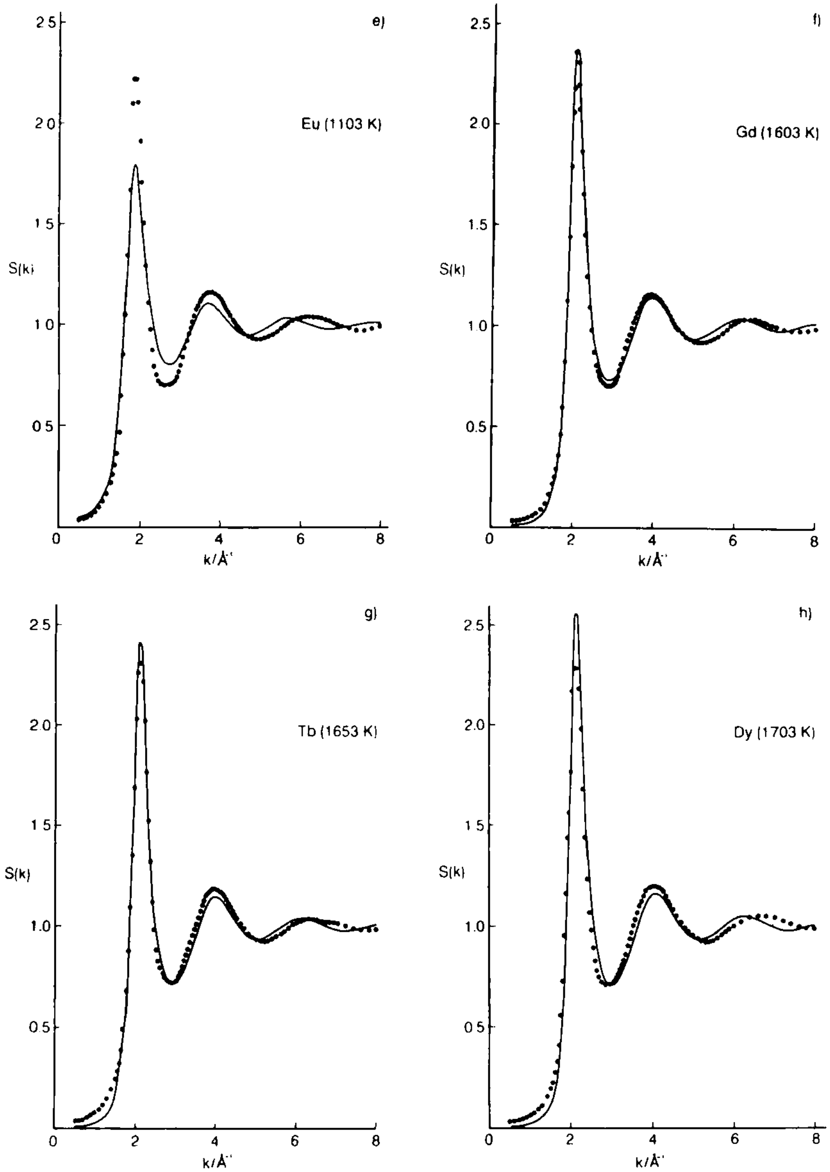

Figure 1 (*continued*) Structure factors of the liquid 4f rare earth metals near melting. Input data, as shown in Table 1, and experimental data, indicated by dots, are taken from Waseda's book[8]. The continuous lines refer to theory (this work). e) Eu; f) Gd; g) Tb; h) Dy.

largest for the WCA method, smallest for the present (MSA) method and intermediate for the hard sphere (Waseda) approach.

With the results given in Table 1 we find that the overall fitting of $S(k)$—shown in Figure 1—is reasonably good except for Eu, Ho, Er and Lu where the theoretical first peaks are too low and first minima less deep than the experimental results.

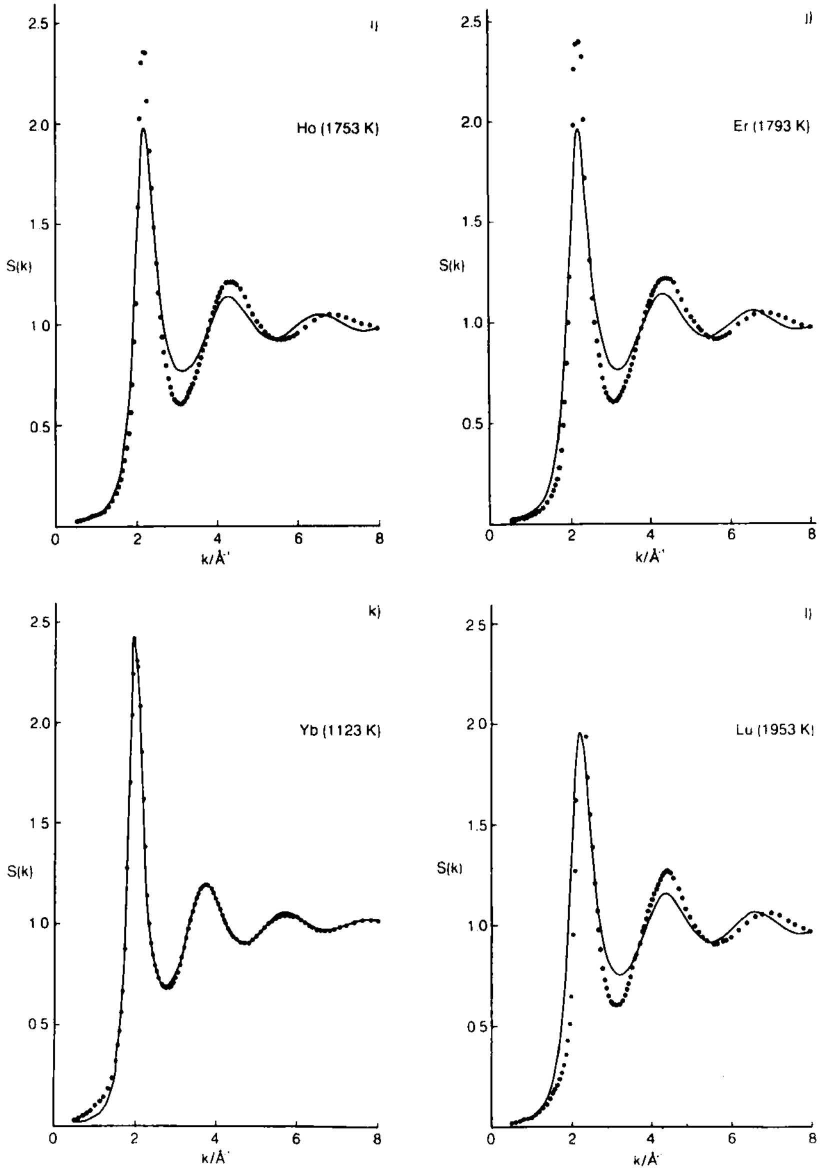

Figure 1 (*continued*) Structure factors of the liquid 4f rare earth metals near melting. Input data, as shown in Table 1, and experimental data, indicated by dots, are taken from Waseda's book[8]. The continuous lines refer to theory (this work). i) Ho; j) Er, k) Yb; and l) Lu.

Nonetheless, the results for $S(k)$ at large momentum transfer are probably the best obtained so far for liquid rare earth metals.

The value of γ varies very little: between 119 for Lu and 440 for Nd, the exceptions are Ho (675), and rising to 1759 for Eu and 2475 for Yb. However, for the reasons discussed below the last two may be regarded as special cases.

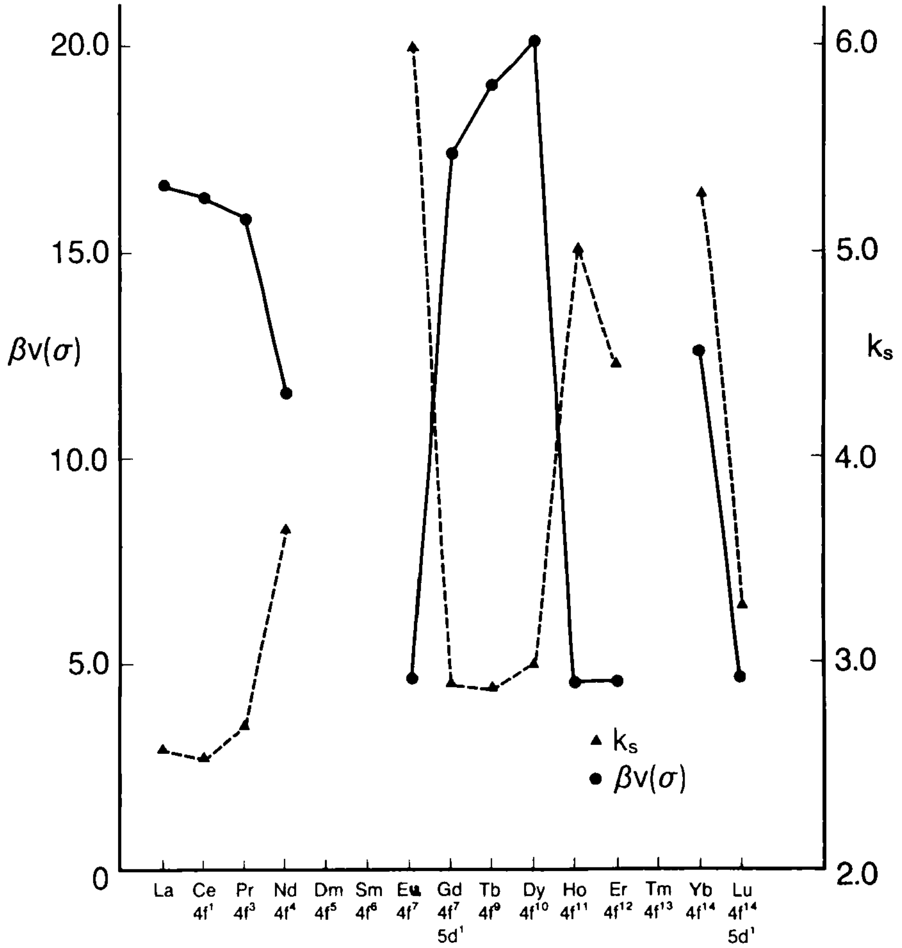

Figure 2 'Softness' parameters k_s (dashed line), and potential $v(r)$ (solid line) at the core $r = \sigma$, in units of $k_B T$, for liquid 4f rare earth metals at melting. The lines do not join for those elements for which experimental $S(k)$ are not available.

The values of the potential at the core, $4.50 < \beta v(\sigma) < 20.10$ like those for the liquid transition metals—are such that the hard core of the potential is never sampled, in contrast to the WCA work where $\beta v(\sigma) \simeq 1$[12]. However, unlike the liquid transition metals, there appear to be no correlation between $\beta v(\sigma)$ and k_s, the 'softness' parameter. Whereas for k_s it is possible to detect a weak trend towards the hardening of the cores (involving La, Ce, Pr, Gd, Tb, Dy and Lu), there is no corresponding pattern for $\beta v(\sigma)$. This is more easily perceived in Figure 2 where both k_s and $\beta v(\sigma)$ are shown. It is only in relation to this weak trend in k_s that our observations would support the qualitative conclusion reached by Waseda[9].

At this point a comment on numerical procedure should be made. In our earlier WCA program involving the rare earth metals and others it was necessary to locate a

Table 2 Comparison of hard sphere diameters obtained from using hard spheres[8], WCA[12] and MSA (this work) analysis.

Rare Earth Metals	*Hard sphere diameters σ/Å*		
	MSA	*Waseda*	*WCA*
La	2.846	3.169	3.195
Ce	2.736	3.035	3.077
Pr	2.796	3.049	3.124
Nd	2.811	3.028	3.117
Eu	3.175	3.526	3.507
Gd	2.920	3.141	3.246
Tb	2.874	3.106	3.204
Dy	2.807	3.010	3.117
Ho	2.828	3.010	3.073
Er	2.833	3.030	3.095
Yb	2.957	3.363	3.459
Lu	2.826	2.985	3.055

minimum in a two-parameter variation. The present calculation carries three independent parameters rather than two, thus the program is obviously more complicated but there is an additional difficult feature. The three parameters varied in the program are σ, k_s and $\beta v(\sigma)$ which together fix γ. No difficulty arises in fixing σ but for k_s and $\beta v(\sigma)$ problems arise. This minimum in the least-square fitting given by Eq. (2.8) is actually approached asymptotically rather than the usual local minimum in the WCA method. Thus there are many combinations of k_s and $\beta v(\sigma)$ that would do equally well to the degree of accuracy of the experimentally derived data. This is especially true for those cases where a poor fit to the data is achieved. The procedure followed was simply to terminate iterations when higher accuracy would imply misleading improvement. For this reason it may be noted that the $\beta v(\sigma)$'s for Ho, Er and Lu are all at the same value which we took as a minimum acceptable value for the model to hold. That assumption, given in the paper by Hayter, Pynn and Suck, was that the hard sphere portion of the potential should be large enough ($\sim 5\ k_B T$) so that it would essentially never be sampled in ion-ion encounters. As the iterations proceed, k_s and $\beta v(\sigma)$ generally vary in opposite ways, one increasing as the other decreases. This character of the parametric variation is readily seen in Figure 2. There are, however, exceptions, especially when the fit to the data is unsatisfactory. In such exceptional cases k_s and $\beta v(\sigma)$ vary in the same direction, both increasing, or both decreasing. The results in Figure 2 for Yb and Lu clearly exhibit this atypical behavior.

From both density and electronic structure data[14] we do not expect the divalent Eu and Yb to fit into any pattern, and they don't. Van Zytveld[14], in his recent excellent review, notes that—with the exception of Eu and Yb—the densities of the liquid lanthanides near melting increase linearly with the atomic number Z. The densities used in our calculations do not follow this behavior and it is a likely source of error in this work. Moreover, the density increases at twice the rate of increase of the atomic weight, implying a contraction of the atomic core with increasing Z, the 'lanthanide contraction'. This is not translated into a corresponding contraction of the effective core diameters of the pseudo-atoms. Instead, as noted in Ref. 12, it appears that a process akin to Hund's rule for filling a subshell operates in deciding the relative sizes of the diameters. The exceptions of Ho and Er are precisely those breaking the pattern of the 'softening' of the repulsive potential, and thus they represent two of the four cases where the fitting of the $S(k)$'s are the poorest.

Acknowledgements

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