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On the origins of the Finnis-Sinclair potentials

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I trace back the origins of the famous Finnis-Sinclair potentials. These potentials mimic the results of tight binding theory through their use of the square root embedding function. From the tentative beginnings of tight binding in the 1930s up to 1984 or so, some of the famous names involved are Bloch, Seitz, Montroll, Friedel, Cyrot-Lackmann, Ducastelle, to name just a few. The application of the method of moments to the description of densities of states and its connexion to the physics of closed paths linking nearest neighbours interacting atoms helped to formalize Friedel's rectangular band model for the d electrons in transition metals. Extension from perfectly periodic structures to defective ones could not be but a slow process due to the change of paradigm for solid state scientists and to the necessary caution to be paid to self-consistency. The British scientists school also contributed significantly in the 80s. Computer progress and pragmatism helped to go from mainly analytical developments to numerical experiments (another change of paradigm). I also digress on various not so well known historical points of interest to this story.

Keywords: Finnis-Sinclair Potentials; tight binding; LCAO; method of moments; second moment approximation; transition metals; semiconductors; Cauchy relations; embedded atom method; molecular dynamics; history of science

1. Introduction

Without going back to ancient Greek models (see [1]), one can say that pair potentials proved to be surprisingly efficient, at least as a first approximation, for metals and ionic crystals since Mie (1903), Grüneisen (1911-1912), Born (with Landé 1918, with Mayer 1932). Yet the consideration that metals are mainly governed by electrons moving more or less freely (Riecke, Drude, Lorentz, Thomson [Clausius-Boltzmann gas], Sommerfeld [Fermi gas] 1928) as in a gigantic molecule which should be treated through the Schrödinger equation (not to mention Dirac's equation) rapidly raised questions. Solving the Schrödinger equation for a large number of atoms in a condensed matter state, however, implies a lot of numerical work (now computer work) which restricts the size of the systems which can be considered. Most physicists have always tried to use, as much as possible, simple models endorsed with some physically interpretable parameters which can be varied at will (for numerical experimentation) and/or fitted versus trustable data (experimental and/or ab initio, when reliability is warranted) for real materials. Simplicity, for understanding, versus realism,

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3 depending on the (complexity of the) question to be addressed: This depends on the
4 conceptual tools, together with the numerical tools, that the physicist may use and master (e.g.
5 irrational numbers and logarithms on one side, and computers on the other side). Conceptual
6 tools for understanding evolve with numerical tools (and technology), and they also evolve in
7 the sense that they may seem odd at first sight and slowly become natural once one gets used
8 to them. They subsequently can be improved. It is this slow evolutionary process that I see at
9 work in what led to what are now called the “Finnis-Sinclair potentials.” My plan will simply
10 follow history, starting in the 30s up to the 80s. I put in appendices some lateral information
11 which I believe is important and not too well-known. I otherwise assume that the reader is
12 acquainted with classical texts such as [2-8].

22 23 **2. The Thirties; first steps, nullified by sensible hesitations**

24
25 In 1935, naturally impressed by the recent breakthrough of Wigner and Seitz (1933, [9]) who
26 had been able to account “quantitatively for the cohesive forces in a typical metal (sodium),”
27 Mott attempted to “give a qualitative discussion, based on the same theory, of some properties
28 of the transition metals” and in particular of the elements nickel and palladium. He considered
29 the outermost s electrons as responsible for the cohesion (and the d electrons as responsible
30 for the magnetic properties) and he estimated to 0.6 the number of s electrons per atom for
31 nickel. In a clever way, he concluded that nickel must have a binding energy greater than that
32 of copper, which agrees with experimental data. Apart from nickel, palladium and platinum,
33 the binding energy of transition metals was not considered and the rest of his article was
34 mainly concerned with the discussion of magnetic susceptibilities and electrical conductivities
35 [10].

36
37 In 1936, H. Fröhlich endorsed this analysis in his textbook for all transition metals in a
38 forcedly odd way (§ 30 of [11]) while Mott and Jones wrote that as far as transition metals are
39 concerned, “no calculations of the binding forces in these metals have yet been made” (*sic*,
40 Chapt. IV, § 3.3 of [12]).

41
42 In 1937, in the second of a set of three highly pedagogical articles, Seitz and Johnson
43 proposed that “as long as the electrons fill depressed zones [the lower states of the bands] we
44 may expect the binding to increase, but when levels which are higher than the atomic states
45 are filled, we may expect the binding to decrease. That is, we expect the binding energy in
46 one of the long periods [$3d$, $4d$, $5d$] to increase with atomic number at first, reach a maximum
47 and then decrease again.” [13]. This simple tight-binding picture naturally implied a number

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2
3 of approximations they perfectly knew about and explained in their series of articles. Seitz
4 only briefly alluded to this scheme in his 1940 book but he re-expressed it, more clearly, in
5 1955 with Wigner in the first volume of the Seitz and Turnbull's Solid State Physics series,
6 stating that in the case of separated p or d bands, "the bands are centered essentially at the
7 value of the atomic level as long as the wave functions are assumed to be composed of atomic
8 functions in the manner [of the tight binding approximation]. The binding is largest for the
9 first electron in each shell in this approximation, is zero for the electron in the middle of the
10 shell, and is negative for the electrons in the second half of the shell. This means that the
11 cohesive energy should attain its maximum near the center of the shell and decrease toward
12 either end." And they provided the reader with a figure of the experimental cohesive energy
13 of the condensed state as a function of the atomic number [14]. This seems to have gone
14 rather unnoticed.

15
16 Also in the US, however (and even in the same State of New York), Slater wrote in
17 1936 that the electrons in the incomplete atomic d shells can be responsible for magnetism but
18 "do not take part in the cohesion," "cannot be engaged in cohesion" [15]. He also wrote that
19 "Overlapping the band of $3d$ electrons is another band, arising from the $4s$ level of the atom,
20 with interactions with the $4p$ and other higher levels. (...) Electrons in this band act like free
21 electrons (...) they contribute strongly to the cohesion." Slater was thus threatening the
22 principle of LCAO calculations that neglected excited atomic states with higher energies but
23 larger overlap and he developed in 1937 a model where the trial wave functions are expanded
24 in terms of plane waves within spheres centred on the nuclei [16]. This celebrated muffin-tin
25 model involves complex calculations the results of which were not easy to interpret (see [17-
26 18]).

27
28 At the end of the thirties, just before the Second World War broke out, discussions
29 about magnetism at an international conference in Strasbourg simply questioned the
30 possibility that d electrons could form bands at all [19-20].

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3. The Sixties; the time of Jacques Friedel and his d band model

After the War, matters settled down, and in 1964, in his Institute of Metals Lecture, J. Friedel
independently re-developed a tight-binding analysis of transition metals concentrating on the
 d band only, in a simpler and more precise way [21]. In this Lecture, Friedel introduced his
famous rectangular d band model: "For all reasonable forms $n_d(E)$ of the d band, one finds
much the same parabolic variation as when $n_d = \text{const.}$ " He then provided the reader with an

equation which does give the parabolic variation of the atomic cohesive energy (with respect to isolated, free atoms, the sublimation energy) with the number of d electrons per atom. (The direct proportionality to the electronic hopping integral between first neighbours β was also clear but the proportionality to the square root of the coordination number of the structure, obviously a secondary point at that time, was missed in the equation simply because the width of the d band was taken as $2|\beta|$, instead of $\sqrt{12}z_c|\beta|$ as it should be for the rectangular d -band where z_c is the coordination number: the number of nearest neighbours per atom. Note that for the real d -band, the width is of the order of $2z_c|\beta|$. For the Gaussian d -band, the width (support) is infinite and one defines instead the standard deviation $\sigma = \sqrt{\text{var}} = \sqrt{\mu_2}$ which equals $\sqrt{z_c}|\beta|$. See Appendix A).

Françoise Cyrot, *née* Lackmann, substantiated her thesis director's assertion about "all reasonable forms $n_d(E)$ " in her PhD thesis (and in [22], in French). For that, she developed the integrals $n_d(E_F) [= \int^{E_F} n_d(E)dE]$ and $E_B(E_F) [= \int^{E_F} E n_d(E)dE]$ for various forms of $n_d(E)$ and numerically plotted the latter versus the former. (Only for the rectangular model can one directly get an analytical formula showing a strict, shifted, parabolic dependence $a[n_d(E_F)-5]^2$.) She used the mathematical formalism of moments (see Appendix A) to approximate the density of states (DOS) of the electrons in transition metals for two reasons: (i) it had already been used to approximate the DOS of the lattice vibrations by Montroll in 1942/3 [23], (ii) in the case of the frequency distribution of the normal states of a Hamiltonian describing a set of discrete atoms containing some degree of disorder, so that the cyclic boundary conditions are no more useful, physicists have found a way to calculate the moments by computing closed graphs, which one can also nicely visualize as closed walks, on the lattice. This was first found (published) by Pirenne in 1958 [24], and, independently at about the same time, by Domb, Maradudin, Montroll and Weiss in 1959 [25], for the study of vibrations on disordered systems (viz. crystals containing isotopes randomly distributed, or mixed binary alloys). In the case of Domb et al., the harmonic interactions were limited to first neighbour interactions (as it is the case in tight binding) and they could develop more applicable relations than Pirenne's general formulae. Thus this naturally was a method of choice for Fr. Cyrot-Lackmann (and Friedel) as she wanted to study the cohesion of liquid transition metals (after discussions with Loup Verlet who was working in the nearest neighbour university building in Orsay) [26]. It was also well suited to calculate surface tensions as there are simply fewer closed graphs related to surface atoms than to bulk atoms.

4. The Seventies (1970) and early Eighties; François Ducastelle and the second moment interaction model

After computing the cohesive energy of a solid, the next idea naturally was to investigate its elastic properties. It was however rapidly realized that the simple rigid band model could not reproduce the bulk modulus (the lower the first nearest neighbour distance, the larger the β overlap interaction, thus the larger the band and the larger the cohesive energy.) [27-28]. It was not possible to go further in a simple way with this band model in order to reproduce even just the main features of the experimental data collected by Gschneider Jr. for the equilibrium atomic volumes, the bulk moduli and the shear moduli which also exhibit parabolic shapes for the transition metal series, at least for the $4d$ and $5d$ series (Gschneider's figures 11, 6 and 3 respectively in his 1964 review paper [29]. The $3d$ series is complicated by magnetism). François Ducastelle, Françoise Cyrot-Lackmann's thesis student, was the first to take this problem over by adding to the purely binding band contribution (purely binding in the simple model adopted) a purely repulsive contribution as a simple sum of repulsive pairwise interactions which he took of the Born-Mayer, $\exp(-pR)$, form, a form particularly suited to the exponential R -form (see Appendix C) of the overlapping integral β chosen by Friedel at interatomic distances in the equilibrium condensed state (on the account that "their [small] number of spherical [nodes] allows them [the atomic d -orbitals] to decrease exponentially as $\exp(-qR)$ at [relatively short] distance from the origin" [30]). With respect to the usual all-pairwise potentials (e.g. Born, Lennard-Jones) it was important to clearly emphasize that the band binding contribution " E_B ne peut pas s'écrire comme une somme de contributions de paires d'atomes bien que μ_2 s'obtienne de cette façon, ceci parce que E_B est proportionnel à $\sqrt{\mu_2}$ et non à μ_2 ." [31]. With this natural and consistent choice of exponential functions, François Ducastelle could develop some relatively simple formulae for the equilibrium parameter, the total cohesive energy at equilibrium, the bulk modulus, and the cubic elastic shear moduli for various elementary atomic structures. For the fcc case for instance, he obtained c_{44} and c' both proportional to $1-2q/p$. François also obtained $c_{44}/c_{12}=(1-2q/p)/(1-2q/3p)$, and, in order to get a good agreement with experimental data, he indicated that p should be comprised between $3q$ and $5q$. Thus, François Ducastelle could reproduce rather well, at least for the fcc transition metals, the non negligible departures from the Cauchy relationship for the cubic structures ($c_{12}=c_{44}$, not to be confused with the $c'=c_{44}$ isotropic relationship), a feature that a pairwise potential could absolutely not reproduce,

whatever its parameterisation (for some comments on the Poisson-Cauchy relations, see Appendix D).

After reproducing the structural and cohesive properties of a solid at, and around its equilibrium state, the following step was to look after the properties of structural defects such as surfaces and vacancies (to start with): their energies of formation and their relaxed atomic structures. For instance it was known that the classical (non oscillatory) all-pairwise atomic potentials give a vacancy energy formation equals to the cohesive energy per atom, which contradicts experimental data for metals by a factor of about three to four, and that they predict an outward relaxation for surfaces when an inward relaxation is usually measured (much less was known about the atomic relaxations around a vacancy). The conceptual difficulty was, however, to go beyond the paradigm of periodicity, so connected to the paradigm of reciprocal space. It is easy to realize, afterwards, that the tight binding and moment approach is actually made for that. It proved difficult to realize it spontaneously at that time and this only came slowly. One had to be sure that no hypothesis or condition was violated, notably self-consistency.

In the manuscript of his thesis, Fr. Ducastelle showed that, because the number of d electrons per atom in the solid does not change under a small elastic transformation, the formula $E_B = -\text{const} \cdot \beta_o \sqrt{\sum_j e^{-2qR_j}}$ is valid for any filling of the d band. In his article, however, he just wrote 'il est facile de voir' and did not even give that formula which, obviously for us now, can be re-written as $E_B = -\text{const} \cdot \beta_o e^{-qR} \sqrt{z_c}$ for a perfect, or only elastically deformed, crystalline structure, and to $E_B(i) = -\text{const} \cdot \beta_o e^{-qR} \sqrt{z_c(i)}$ for every atom i in a complex structural defect provided electrical neutrality is maintained at first order of approximation for each atom, which is true in metals thanks to metallic screening. It was simply beyond preoccupations in 1970, and even in the simple case of perfect crystal, the (already solved) problem was raised eighteen years later by Ackland, Finnis and Vitek about the Gaussian formulation [32]. The choice of a Gaussian $n_d(E)$, instead of the rectangular function originally used by Friedel in 1964, actually rendered the 'il est facile de voir' less straightforward than in the rectangular case where $E_B = -[(n_d^2 - 10n_d)/20] \cdot |\beta| \sqrt{z_c}$ which obviously gives $E_B = -\text{const} \cdot |\beta| \sqrt{z_c}$ if n_d remains constant per atom (see Appendix A). The choice of a Gaussian $n_d(E)$ came from the fact that it is the first level of the Edgeworth series which can naturally include higher order moments [22]. Within the second moment approximation, Ackland et al. [32] provided a mathematical demonstration of the validity of

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3 the proportionality to $\sqrt{\mu_2(i)}$, and thus to $\sqrt{z_c(i)}$, in any local environment which preserves
4 the local charge neutrality and the original symmetry of the local DOS (only compression or
5 stretching by a constant factor, plus global shift to maintain charge neutrality).
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9 Considering electrical neutrality at the atomic level even around a vacancy also means
10 neglecting the Friedel charge oscillations, which is entirely valid if one is not trying to analyse
11 them, as we now know for sure. Might have it represented a conceptual difficulty for the
12 students of Friedel in spite of Friedel's own pragmatism? It simply was not that obvious, and,
13 whereas some people made it right in the details of their calculations, some people made it
14 wrong. Sutton et al.'s article, with a first principles background, masterly settled the point in
15 1988 [33].
16
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19 Yet, in 1976, Allan & Lannoo had already considered these problems, in an article
20 which contains a discussion of the influence of self-consistency on the relaxation near a
21 vacancy in transition metals [34]. They had also obtained a very simple formula for the fcc
22 vacancy formation energy: $E_{\text{vac}} \sim E_{\text{coh}} \cdot (1-2q/p)/(2[1-q/p])$ (to first order in $1/z_c=1/12$). E_{coh} is
23 the corresponding cohesive energy, with respect to neutral free atoms), which gives a ratio
24 $E_{\text{vac}}/E_{\text{coh}}$ comprised between 0.25 and 0.375 for $3q \leq p \leq 5q$, which sensibly agrees with
25 experimental values (first nearest neighbour pair potentials give $E_{\text{vac}} = E_{\text{coh}}$).
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29 Allan and Lannoo [34-36], Gordon, Cyrot-Lackmann and Desjonquères [37], Masuda
30 and Sato [38], Gupta [39], Desjonquères and Spanjaard [40-41], Tomanek and Bennemann
31 [42]: They all used Ducastelle's model to investigate more or less complex systems, including
32 adatoms, small clusters, screw dislocation, carrying out some more or less extended relaxation
33 on the atomic positions near the defect, always trying to keep closed form analytical formulae
34 as much as possible. When it was not possible, as in the case of the screw dislocation in dilute
35 bcc transition metal alloys, Masuda and Sato had everything to "calculate the total energy as a
36 function of the atomic displacements" and "the atoms in the crystallite [were] relaxed along
37 the screw dislocation." [38]
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51 5. 1984; the Finnis-Sinclair article

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53 So what was new with Finnis and Sinclair 1984 [43], who acknowledged they chose " $f(\rho)$ to
54 be $\sqrt{\rho}$, so as to mimic the result of tight-binding theory"? I see several important points (from
55 a to f):
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59 a . The title: "A simple empirical N-body potential for transition metals." By contrast with
60 previously mentioned articles, they do not announce the calculation of a specific property but

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3 they present a tool.

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5 *b.* Their pragmatism: “the present approach is empirical”, “the consequences of the form of
6 the model (...) do not depend on the physical interpretation.” One may compare this attitude
7 with Newton’s “hypotheses non fingo.” Pragmatism also includes some amount of anti-
8 Cartesianism.
9

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11 *c.* A general program: “for the purpose of atomistic simulation”, with explicit consideration
12 for forces at the atomic level: “In order to perform atomistic simulations of crystals containing
13 defects it is essential to have a rapid algorithm for calculating the force on each atom.” They
14 do provide the reader with general analytical formulae for calculation of forces. This will
15 allow for Molecular Dynamics, not just static minimization. (On MD simulations using *n*-
16 body potentials, see Appendix E.)
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19 *d.* The Zeitgeist: Daw and Baskes had just published their two articles [44-45]. So it was in
20 the air. In an interview in August 2000, Michele Parrinello declared that in 1983 “we invented
21 what is called the glue potential, on which Ercolessi wrote his thesis. He was drafted for
22 military service, and the work was stopped for a year and a half. During that time other people
23 had similar ideas, and applied them in metals. So due to the draft we lost time, and bit of
24 priority on this problem, but that’s life.” [46]
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33 Yet there are obvious philosophical differences between these three approaches:

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35 *(i)* Ercolessi, Parrinello and Tosatti declared that “although further theoretical justifications of
36 this scheme can be found in the so-called embedded-atom method,” they did “not believe that
37 a truly first principles derivation can be given” [47] and they worked out purely empirically
38 constructed analytical functions, carried out once, for gold [48].
39
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41
42 *(ii)* Daw and Baskes used purely numerical functions deduced from first principle calculation
43 or via a semi-empirical approach. These functions can only be tabulated and plotted.
44
45

46
47 *(iii)* Finnis and Sinclair used simple analytical functions, with the square root embedding
48 function, “so as to mimic the result of tight-binding theory.”
49

50 The origin of Daw and Baskes Embedded Atom Method has later been traced back,
51 probably by Foiles [49-50], to Friedel 1952 impurity-in-jellium model [51] (see Appendix F).
52 The basic idea from which Daw and Baskes drew on is that an atom in a metallic environment
53 does not feel the detailed structure of the nearby atoms due to the effective screening in
54 metallic systems. Each atom is considered as hosted in a homogeneous gas (LDA spirit) and
55 its energy becomes a functional of the local host electron density in which it is immersed.
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57 With this approach which only considers the local electronic density, it is difficult to
58 distinguish between fcc and hcp structures for instance. A pragmatic way to go is to consider
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3 under the embedding function, square root or whatever, sums of pairwise interactions which
4 include the third neighbours. By contrast, interpreting the square root as a signature of second
5 moment approximation allows one to see a more sophisticated way to go further in principle,
6
7 by trying to include more moments in the formalism.
8
9

10 *e.* Given the pragmatism of the Finnis-Sinclair approach, and the similarity with the
11 embedded atom method, the FS approach was soon extended to noble metals [52] (In 1976,
12 Allan and Lannoo had already noted that the Ducastelle model works pretty well for noble
13 metals [34]).
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17 *f.* The fast increase of computer power allowed for the fulfilling of the program about
18 “atomistic simulation” in the following years (see Appendix E).
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22 **6. Short conclusion; for a continuing story**

23
24 The way from the perfect crystal and the so useful and wonderful reciprocal space
25 (experimentally accessible for almost a century thanks to X-rays for instance) to the real space
26 and the defects at the atomic level proved to be a long path which demanded several moments
27 of reflexions. It is clear that there is still place for continued action, on an at least bimodal
28 way based on theory and on practice, as this special issue shows it.
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38 **Acknowledgments**

39 I thank Professor Jacques Friedel, as well as François Ducastelle, for many invaluable
40 discussions, by post mail and email. I also wish to thank the library department of the École
41 Polytechnique for providing me with many ancient articles and books.
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47 **Appendix A: the origins of the moments and the method of moments**

48
49 A known positive function (reasonably well behaved, e.g. a weight function, a probability
50 distribution function) can be geometrically described (analysed) through its moments (which
51 are usually normed and centred, but attention must be paid if a more general formalism is
52 adopted). The zeroth order one corresponds to its surface (its mass, usually normed to 1), the
53 first order moment gives the centre (centre of mass, the mean value of the weighted X -line),
54 with the second order moment one can get a measure of the ‘width’ of the function (the root
55 mean square deviation with respect to the chosen origin, directly the standard deviation if it is
56 with respect to the centre of the function), with the third order moment combined with the
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previous one one can get a measure of the asymmetry of the function, and with the fourth order moment one can have some indication on the mono or bimodality of the function.

If one does not know the function by itself, but can have access to its first moments (one way or another), one then has methods to approximate that function although the approximation is not unique and may not be too good if one is after a precise description of the function (this is usually not the case at the beginning of a new field of research, as with Friedel in the 60s, but it rapidly turned out to be in the 80s). The expression of a distribution as a function of its moments does not constitute a converging series at all. When the number of moments gets large, an elegant solution to that so-called moment problem is based on the continued fraction technique. This is a mathematical problem which goes back to I.J. Bienaymé (1852) and P.L. Čebyšev who is the founder of the use of continued fractions for the method of moments (Tchebychef 1874, his disciple Markov in 1884, and Stieltjes, independently, in 1894). The solution is also closed to the recursive method (Lanczos' method, see [3-4], and all contributions by Heine, Haydock, etc., in [53]). For the historical connection between continued fractions and Padé approximants, see [54].

The 'second moment' is the second order moment, thus the third moment. As usual, beware of notations and conventions, normalisation (yes or not, per atom, or even per electronic state if they are all equivalent.) and choice of origin (e.g. centred or not).

With the following notation, $m_n = \int X^n f(X)dX$; $\alpha_n = \frac{1}{m_0} \int X^n f(X)dX = \overline{X^n}$ and $\mu_n = \frac{1}{m_0} \int (X - \alpha_1)^n f(X)dX = \overline{x^n}$ with the centred variable $x = X - \alpha_1$, I simply recall the following classical results (e.g. see [55]):

$\mu_0 = 1$	$\mu_1 = 0$	$\mu_2 = \overline{x^2}$	$\mu_3 = \overline{x^3}$	$\mu_n = \overline{x^n}$
$\alpha_0 = 1$	$\alpha_1 = \overline{X}$	$\alpha_2 = \mu_2 + \alpha_1^2 = \mu_2 + \overline{X}^2$	$\alpha_3 = \mu_3 + 3\alpha_1\mu_2 + \alpha_1^3$	α_n
$m_0 = S$	$m_1 = S\alpha_1$	$m_2 = S\alpha_2$	$m_3 = S\alpha_3$	$m_n = S\alpha_n$

From the notation $\mu_2 : \sigma^2$, one gets $\sigma^2 = \alpha_2 - \alpha_1^2 = \overline{X^2} - \overline{X}^2$.

When the distribution is known, the μ_n , because they are centred, are the easiest moments to calculate.

The second moment approximation does not mean that there is a series which is truncated to its second moment (or third term). It means that no other parameter is available.

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3 Yet, with only three moments, the distribution can be rectangular, Gaussian, parabolic, ... For
4 instance let us consider a rectangular distribution of surface S , of width w and centred on M ,
5 and a Gaussian (Laplace-Gauss) distribution of surface S , of half 'width' σ at $1/\sqrt{e}$ height and
6 centred on M . These two distributions being symmetric with respect to their centres M , their
7 odd centred moments are null. Their even moments μ_{2n} are $w^{2n}/[(2n+1)2^{2n}]$ for the rectangular
8 distribution, and $\sigma^{2n}(2n)!/(2^n n!)$ for the Gaussian distribution. Thus nothing more than three
9 parameters, S , M and w , or S , M and σ , are required to entirely describe these two
10 distributions and their moments. Conversely, three parameters, m_0 , m_1 (or α_1) and m_2 (or α_2)
11 or μ_2) can define a rectangular or a Gaussian distribution. These two distributions obviously
12 have different shapes (and different moments beyond μ_2 , e.g. μ_4 equals $144\mu_2^2/90$ for the
13 rectangular case, and $3\mu_2^2$ in the Gaussian case).

14 For an elementary crystal which can be described by a tight-binding Hamiltonian, one
15 considers that every atom has m_0 equivalent electronic state available (10 for the d states, spin
16 state included), and the {Pirenne—Domb et alii—Cyrot-Lackmann}-theorem gives $\alpha_1 = E_0$,
17 the inner atomic level which is equal to the atomic level E_{at} plus a shift α due to the fact that
18 the atoms are not isolated, and $\mu_2 = z_c \beta^2$ (there are z_c closed walks which go to a first
19 neighbour and thus contribute, way and return, $\beta \cdot \beta$). Assuming a rectangular distribution, one
20 thus gets $w^2/12 = z_c \beta^2$ hence $w = \sqrt{12} \sqrt{z_c} |\beta|$ whereas $n_d(E_F) = \int_{E_0-w/2}^{E_F} A dE = \frac{10}{w} [e_F + w/2]$ (since
21 $S = Aw = m_0 = 10$ and noting e the centred variable $e = E - E_0$) and
22 $E_B = \int_{E_0-w/2}^{E_F} (E - E_{at}) A dE \sim \frac{10}{2w} [e_F^2 - (w/2)^2]$ if one neglects the shift α for the sake of clarity,
23 which gives, after some simple algebraic manipulations, $E_B = -2.5w + \frac{w}{20} [n_d(E_F) - 5]^2$, a
24 shifted parabola in $n_d(E_F)$, and also a linear function in w , hence $E_B = -\text{const} \cdot |\beta| \sqrt{z_c}$. Assuming
25 a Gaussian distribution does not alter the conclusions but makes the demonstration purely
26 numerical for the parabolic shape, and more subtle (at least to my taste) for the linear
27 dependence in $|\beta| \sqrt{z_c}$. In his truly remarkable sometimes intuitive way, Friedel 'knew' in
28 1964 that these results would not depend much on the shape of $n_d(E)$. Yet, as far as I am
29 concerned, I can understand it only through the demonstrative work carried out by Fr. Cyrot-
30 Lackmann.

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Note on the bimodality indicator

Jean-Pierre Gaspard [3-4] noticed that the ratio $\tilde{b} = (\mu_4\mu_2 - \mu_3^2 - \mu_2^3)/\mu_2^3$, which can be deduced from the first two terms of the continued fraction of the resolvent of the distribution function, gives some indication on the mono or bimodality of a distribution. A distribution with $\tilde{b} \gg 1$ is monomodal whereas a distribution with $\tilde{b} \ll 1$ is bimodal. It is tempting to propose a critical value for \tilde{b} . However such a critical value does not exist in a universal way. Just to give two examples, it is 0.8 for the symmetrical beta law $([x(1-x)]^{a-1})$, for $0 \leq x \leq 1$, a being a real number > 0) but for the symmetrical mixture of two equivalent Gaussians differing only by their centres, it is 1.5. The case of a non symmetrical distribution will be more difficult to decide. Let us also note that, using Pearson's coefficients $\beta_1 = \mu_3^2/\mu_2^3$ and $\beta_2 = \mu_4/\mu_2^2$, one has $\tilde{b} = \beta_2 - \beta_1 - 1$.

Some original quotations which introduced the moments:

Marin Mersenne (French monk and universal scientist, well known for being in touch with almost all savants of his time), in his free translation/adaptation in 1634 of the not yet published lectures of Galileo Galilei on Mechanics at the University of Padua in the 1590s: "Le *moment* est l'inclination du mefme corps, lors qu'elle n'est pas feulement confidérée dans ledit corps, mais conioinctement avec la fituation qu'il a fur le bras d'un leuier, ou d'une balance." [56]

Galileo Galilei, in *Le Mecaniche*, posthumously published in Ravenna in 1649: "Momento è la propensione di andare al basso, cagionata non tanto dalla gravità del mobile, quanto dalla disposizione che abbino tra di loro diversi corpi gravi" [57]

Irénée-Jules Bienaymé (1852): "(...) si l'on appelle μ_Σ la moyenne des puissances Σ de toutes les erreurs possibles, on aura $\int \varepsilon^\Sigma d\varepsilon \varphi(\varepsilon) = \mu_\Sigma$ " [58]

Pafnouty Lvovitch Tchebychev (1874): "En cherchant à tirer tout le parti possible sur les valeurs limites de l'intégrale $\int_a^h f(x)dx$ des valeurs des intégrales $\int_A^B f(x)dx$, $\int_A^B xf(x)dx$, $\int_A^B x^2 f(x)dx$, $\int_A^B x^m f(x)dx$, où l'on a $A < a$, $B > b$, et où $f(x)$ reste positive, je suis parvenu à

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3 reconnaître que ces recherches conduisent à des théorèmes d'un nouveau genre, concernant le
4 développement de l'expression $\int_A^R \frac{f(x)}{z-x} dx$ en fraction continue, qui joue un si grand rôle dans
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7 la théorie des séries." [59]
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11 Thomas-Jan Stieltjes (1894): "Considérons sur une droite infinie une distribution de masse
12 (positive), la masse m_i se trouvant concentrée à la distance ξ_i de l'origine. La somme $\sum m_i \xi_i^k$
13 peut être appelée le *moment* d'ordre k de la masse par rapport à l'origine." [60]
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28 **Appendix B: on Tight Binding and LCAO**

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30 Felix Bloch demonstrated (in much more details than some forerunners as Houston, Strutt,
31 Frenkel, and quite independently) that if the ionised atoms are positioned regularly, as in a
32 crystal, then, for the electrons in such a periodic lattice, there are solutions of Schrödinger's
33 equation in the form of plane waves that describe electrons travelling in any direction through
34 the crystal without being scattered [61]. The Bloch plane-wave solutions are more
35 complicated than the de Broglie wave of an electron in free space, but a wave-vector \mathbf{k} may
36 still be defined: one has to deal with de Broglie waves, "die im Rhythmus des Gitteraufbaus
37 moduliert sind." Exact solutions for any particular choice of the periodic potential $V(\mathbf{r})$ (: the
38 interaction potential between the conduction electrons and the lattice) are probably impossible
39 to find and Bloch worked out exact solutions in a limit case he knew from his time in Zürich
40 where he, and Heitler and London enjoyed walking together. F. Bloch drew on the idea that
41 Heitler and London had used on their treatment of the hydrogen molecule, that of constructing
42 electron wave functions starting from a basis of unperturbed single-atom ground-state
43 orbitals. F. Bloch called it the limit case of stark gebundener Elektronen (strongly bound
44 electrons), which came to be know as tight-binding approximation. In his 1931 article, Erich
45 Hückel extensively referenced F. Bloch [62]. At the request of their common director
46 Heisenberg, Peierls, among many other things, worked out the solution for a nearly free
47 version of $V(\mathbf{r})$, instead of the tight-binding version chosen by Bloch, and was delighted to get
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3 some similar results which were thus likely to be independent on the details of the interactions
4 of the electrons with the atoms. A.H. Wilson developed the band theory further (see [63-65]).
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7 Wigner and his student Seitz blurred the landscape in 1933 when they explicitly
8 considered the work of Bloch as mainly based on the hypothesis of free electrons in chemistry
9 [9]. Mott and Jones coined the English expression ‘tight binding’ approximation in their 1936
10 book [12]. Friedel and his co-workers always quoted Hückel for the tight-binding
11 approximation.
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15 Yet, in 1931, referring to F. Bloch 1928, Erich Hückel wrote: “Es lassen sich dann die
16 Eigenfunktionen eines Elektrons durch Linearkombinationen der Eigenfunktionen des
17 Elektrons bei getrennten Atomen annähern.” (p. 219 of [62]). And, in 1955, Reitz clearly
18 wrote: “the *linear combination of atomic orbitals*, or *Bloch*, or *tight binding method*. This
19 technique was first proposed for solids by Bloch.” (page 16 of [66])
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25 It must be recognized that Bloch’s name, because of Bloch’s theorem, conveys the idea
26 of periodicity, and Fourier transforms. By contrast, because Hückel dealt with finite size
27 molecules, his name conveys the idea of as distorted as you like configurations with a real
28 space approach (even if Hückel happened to also use Bloch’s periodicity trick because he
29 actually dealt with benzene, a cyclic ‘aromatic’ molecule!). It is also probably difficult to
30 comprehend that some electrons may be delocalized without being totally free. The most
31 relevant picture here is that of itinerant electrons, hopping from one atom to the next, but not
32 necessarily forming a homogeneous jellium between the atoms as free electrons do.
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40 Lennard-Jones is usually given as the founder of the LCAO method in 1929 [67]
41 although this was the way of doing at that time: Hund 1927 onward, Mulliken 1928, Lennard-
42 Jones 1929. Mulliken formalized the technique and introduced the English term ‘LCAO’ in
43 1935 [68].
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47 There is a difference in spirit between Heitler and London 1927 and the so-called Hund-
48 Mulliken approach, at least in their premises. Heitler & London 1927 start with atomic
49 orbitals, AOs, (e.g. $\varphi_A(\mathbf{r})$ and $\varphi_B(\mathbf{r})$) which they combine, through multiplications and
50 additions, to generate symmetrical and antisymmetrical functions. The building blocks of the
51 Hund-Mulliken approach are LCAOs, sums and differences of atomic orbitals (e.g.
52 $\varphi_A(\mathbf{r})+\varphi_B(\mathbf{r})$ and $\varphi_A(\mathbf{r})-\varphi_B(\mathbf{r})$) which are then combined to generate symmetrical and
53 antisymmetrical functions. These building blocks are more appropriate when the atoms are
54 relatively close together, yet still retaining some of their atomic character: this is the spirit of
55 the ‘tight binding’ approach.
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3 Tight binding has also been successfully developed for covalent materials by Friedel,
4 Leman, Lannoo, Allan, Gaspard, and others with the use of moments. We are dealing here
5 with s and p electronic states, which are quite different in nature from the atomic like d states.
6 But because of the sp^3 hybridization, these materials crystallize in the cubic diamond atomic
7 structure, which is an open structure so that the influence of the second neighbours can be
8 neglected in a first approximation with respect to the influence of the first neighbours. A tight
9 binding treatment is relevant, and successful. The electrons are nevertheless free to move
10 from one atom to any other through the covalent bounds and the $E(k)$ dispersion for silicon is
11 very close to the free electron dispersion at small k . The cubic diamond materials have been
12 the first for which n -body potentials have been developed [69], although for a completely
13 different reason. The tetrahedral angles between the sp^3 bonds is a fundamental of the cubic
14 diamond structure and can only be reproduced with three body terms with explicit angular
15 dependence (and it takes three points to define an angle). The Cauchy relations are violated
16 for cubic diamond materials for two reasons: the interactions are not pairwise and the atoms
17 are not centres of symmetry. The Cauchy discrepancy being negative, an embedded function
18 of the usual type cannot be expected to work. The presence of explicit angular dependent
19 terms seems necessary.
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Appendix C: exponential or power laws?

42 The exponential form of the overlap, or transfer or hopping or bond, integral, has been chosen
43 historically, in part because of the widespread use of the “Slater” orbitals [70]. Ab initio
44 calculations that the dependence should rather be of the inverse power form [71-72].
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48 In the immediate vicinity of the equilibrium first neighbour distance R_o , it does not
49 matter since one has $e^{-\kappa R} \sim cR^{-n}$ with $n = \kappa R_o$ and $c = (R_o/e)^n$. If one wants to stretch the
50 bonds further, i.e. to extend the validity of the overlap law, both solutions fail and pragmatism
51 must prevail, especially for the smoothing of the function down to zero (e.g. see §7.3.2 of
52 [8]).
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Appendix D: on the Cauchy relations

Following the mechanical school of Navier, Poisson, Cauchy, Clausius and Saint-Venant, one should have special relations between elastic constants which A.E.H. Love called Cauchy relations in the historical introduction of his famous treatise on elasticity more than a century ago [73]. These relations are consequences of the hypothesis of interactions between atomic point centres, together with other hypotheses such as pairwise interactions, atoms being symmetry centres of the structure, and no constraints at zero deformation. They proved to be incompatible with experimental measurements (once properly made..., for instance by W. Voigt) so that the atomic hypothesis was contested by positivist anti atomists such as Pierre Duhem, by no means an obscurantist. He was right in the sense that the real atoms are not point centres with no internal structure. From an opposite point of view, in the sixth volume of the Handbuch der Physik series in 1928, J.W. Geckeler wrote that for the elementary metals which violate the Cauchy relations, one must conclude that their atomic structure is not just a simple (Bravais) lattice. Still later on, Raman and his disciples in India, and Laval in France were to oppose Born about the number of independent elastic constants for diamond.

Cauchy's name is also associated to the opposite mechanical school, viz. the continuous mechanics tradition. The appellation Poisson-Cauchy relations would be more fitted, from an historical point of view.

Daw and Baskes noted that the positive curvature of the embedding function implies positive Cauchy discrepancies. Finnis and Sinclair reproduced the same remark, noting that it is the case for the square root function. Thus for metals with negative discrepancies, such as rhodium and iridium, it means that these metals have some basic properties which are not taken into account by the EAM model, for instance explicit angular dependant terms (hence the MEAMs: modified EAMs).

DFT ab initio calculations, in full electrons or with pseudopotentials, only started in the eighties, with sometimes only a moderate success as far as the calculation of elastic constants is concerned (see [1]).

Appendix E: the first MD simulations with n-body potentials

As far as I know, the first MD simulation with a metallic n-body potential was carried out by S.M. Foiles in 1985 with an EAM potential for liquid transition and noble fcc metals (Ni, Pd, Pt, Cu, Ag, and Au) [74].

It is worth noting that at the same time, Stillinger and Weber designed an n-body potential for silicon, with explicit angular dependence, based on experimental and ab initio data, and also performed Molecular Dynamics calculations to check the liquid state [75].

Ercolessi, Parrinello and Tosatti in 1988 (published) performed MD simulations with their glue gold model in order to check the melting temperature of their model [52].

Rosato, Guillope and Legrand in 1989 are the first who carried out MD simulations with FS-like potentials, with Ducastelle's exponential functions, on fcc transition metals [76].

For sake of completeness, I also mention the MD simulations of systems of rigid molecules: When atoms of rigid molecules interact together through relatively long ranged Van der Waals interactions, one can say that the molecules, which are the elementary (rigid) bodies of the system, interact together through n-body potentials. The first MD simulation of this kind is by Barojas, Levesque and Quentrec in 1973 [77]. The interaction model was described in 1967 by Sweet and Steele [78].

For a short introduction to atomistic simulations, Monte Carlo Metropolis and Molecular Dynamics, with some historical information, see [79].

Appendix F: on the origins of the EAM

Stephen Foiles wrote in 1996 ([50], + see [49]) that "the idea of an embedding energy was first suggested by Friedel [51] and later developed further by Nørskov and Lang [effective medium theory 1980] and by Stott and Zaremba [quasi-atom concept 1980]."

In the late 40s, J. Friedel carried out the first numerical study of grain boundaries at the atomistic level (see [80]). Yet, a little disappointed by the crudeness of the pairwise interatomic potentials he had had to use, he decided to learn more about electronic interactions in metals and was introduced by his cousin Ch. Crussard to N.F. Mott in Bristol. There he also met Charles Frank, and his future wife.

In 1936, Mott, concerned with dilute solid solutions (metallic alloys, Hume-Rothery

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3 electron concentration rule (the famous 21/13 ratio, in 1926), influence on electric resistivity)
4 had considered the problem of local screening of charges around (highly dispersed) impurities
5 in a metallic matrix, notably when the dissolved and solvent metals do not occupy the same
6 column in the periodic table, e.g. when an atom of zinc or aluminium is dissolved in copper.
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11 “The extra electrons of the dissolved atom must be regarded as belonging to the lattice rather
12 than to the atom. We should therefore expect the dissolved atom to carry an extra positive
13 charge z , equal to 1 for zinc, 2 for aluminium” [81]. Friedel ([51, 82]) modified Mott’s rapidly
14 decaying solution (à la Debye-Hückel) into a less rapidly decaying solution with oscillations
15 which later came to be known as ‘Friedel oscillations’.

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19 The conceptual difficulty master was to consider the extra electrons of the impurity as
20 given to the lattice, thus unbound, and yet to have the jellium respond as a local charge
21 concentration (electron polarization cloud). One indeed finds in Friedel 1952 the idea that “an
22 impurity atom is embedded in a regular lattice”, and that the perturbation is only local (then,
23 self consistently, that embedded atom can only depend on its local environment).

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28 It must however be recognized that the lack of simple guidelines, except complex ab
29 initio calculations or optimization fitting on empirical data, is not in the spirit of J. Friedel’s
30 approach.
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41 **Appendix G: unabridged references**

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On the origins of the Finnis-Sinclair potentials

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On the origins of the Finnis-Sinclair potentials

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I trace back the origins of the famous Finnis-Sinclair potentials. These potentials mimic the results of tight binding theory through their use of the square root embedding function. From the tentative beginnings of tight binding in the 1930s up to 1984 or so, some of the famous names involved are Bloch, Seitz, Montroll, Friedel, Cyrot-Lackmann, Ducastelle, to name just a few. The application of the method of moments to the description of densities of states and its connexion to the physics of closed paths linking nearest neighbours interacting atoms helped to formalize Friedel's rectangular band model for the d electrons in transition metals. Extension from perfectly periodic structures to defective ones could not be but a slow process due to the change of paradigm for solid state scientists and to the necessary caution to be paid to self-consistency. The British scientists school also contributed significantly in the 80s. Computer progress and pragmatism helped to go from mainly analytical developments to numerical experiments (another change of paradigm). I also digress on various not so well known historical points of interest to this story.

Keywords: Finnis-Sinclair Potentials; tight binding; LCAO; method of moments; second moment approximation; transition metals; semiconductors; Cauchy relations; embedded atom method; molecular dynamics; history of science

1. Introduction

Without going back to ancient Greek models (see [1]), one can say that pair potentials proved to be surprisingly efficient, at least as a first approximation, for metals and ionic crystals since Mie (1903), Grüneisen (1911-1912), Born (with Landé 1918, with Mayer 1932). Yet the consideration that metals are mainly governed by electrons moving more or less freely (Riecke, Drude, Lorentz, Thomson [Clausius-Boltzmann gas], Sommerfeld [Fermi gas] 1928) as in a gigantic molecule which should be treated through the Schrödinger equation (not to mention Dirac's equation) rapidly raised questions. Solving the Schrödinger equation for a large number of atoms in a condensed matter state, however, implies a lot of numerical work (now computer work) which restricts the size of the systems which can be considered. Most physicists have always tried to use, as much as possible, simple models endorsed with some physically interpretable parameters which can be varied at will (for numerical experimentation) and/or fitted versus trustable data (experimental and/or ab initio, when reliability is warranted) for real materials. Simplicity, for understanding, versus realism,

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3 depending on the (complexity of the) question to be addressed: This depends on the
4 conceptual tools, together with the numerical tools, that the physicist may use and master (e.g.
5 irrational numbers and logarithms on one side, and computers on the other side). Conceptual
6 tools for understanding evolve with numerical tools (and technology), and they also evolve in
7 the sense that they may seem odd at first sight and slowly become natural once one gets used
8 to them. They subsequently can be improved. It is this slow evolutionary process that I see at
9 work in what led to what are now called the “Finnis-Sinclair potentials.” My plan will simply
10 follow history, starting in the 30s up to the 80s. I put in appendices some lateral information
11 which I believe is important and not too well-known. I otherwise assume that the reader is
12 acquainted with classical texts such as [2-8].

22 23 **2. The Thirties; first steps, nullified by sensible hesitations**

24
25 In 1935, naturally impressed by the recent breakthrough of Wigner and Seitz (1933, [9]) who
26 had been able to account “quantitatively for the cohesive forces in a typical metal (sodium),”
27 Mott attempted to “give a qualitative discussion, based on the same theory, of some properties
28 of the transition metals” and in particular of the elements nickel and palladium. He considered
29 the outermost *s* electrons as responsible for the cohesion (and the *d* electrons as responsible
30 for the magnetic properties) and he estimated to 0.6 the number of *s* electrons per atom for
31 nickel. In a clever way, he concluded that nickel must have a binding energy greater than that
32 of copper, which agrees with experimental data. Apart from nickel, palladium and platinum,
33 the binding energy of transition metals was not considered and the rest of his article was
34 mainly concerned with the discussion of magnetic susceptibilities and electrical conductivities
35 [10].

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37 In 1936, H. Fröhlich endorsed this analysis in his textbook for all transition metals in a
38 forcedly odd way (§ 30 of [11]) while Mott and Jones wrote that as far as transition metals are
39 concerned, “no calculations of the binding forces in these metals have yet been made” (*sic*,
40 Chapt. IV, § 3.3 of [12]).

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42 In 1937, in the second of a set of three highly pedagogical articles, Seitz and Johnson
43 proposed that “as long as the electrons fill depressed zones [the lower states of the bands] we
44 may expect the binding to increase, but when levels which are higher than the atomic states
45 are filled, we may expect the binding to decrease. That is, we expect the binding energy in
46 one of the long periods [*3d*, *4d*, *5d*] to increase with atomic number at first, reach a maximum
47 and then decrease again.” [13]. This simple tight-binding picture naturally implied a number

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3 of approximations they perfectly knew about and explained in their series of articles. Seitz
4 only briefly alluded to this scheme in his 1940 book but he re-expressed it, more clearly, in
5 1955 with Wigner in the first volume of the Seitz and Turnbull's Solid State Physics series,
6 stating that in the case of separated p or d bands, "the bands are centered essentially at the
7 value of the atomic level as long as the wave functions are assumed to be composed of atomic
8 functions in the manner [of the tight binding approximation]. The binding is largest for the
9 first electron in each shell in this approximation, is zero for the electron in the middle of the
10 shell, and is negative for the electrons in the second half of the shell. This means that the
11 cohesive energy should attain its maximum near the center of the shell and decrease toward
12 either end." And they provided the reader with a figure of the experimental cohesive energy
13 of the condensed state as a function of the atomic number [14]. This seems to have gone
14 rather unnoticed.

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16 Also in the US, however (and even in the same State of New York), Slater wrote in
17 1936 that the electrons in the incomplete atomic d shells can be responsible for magnetism but
18 "do not take part in the cohesion," "cannot be engaged in cohesion" [15]. He also wrote that
19 "Overlapping the band of $3d$ electrons is another band, arising from the $4s$ level of the atom,
20 with interactions with the $4p$ and other higher levels. (...) Electrons in this band act like free
21 electrons (...) they contribute strongly to the cohesion." Slater was thus threatening the
22 principle of LCAO calculations that neglected excited atomic states with higher energies but
23 larger overlap and he developed in 1937 a model where the trial wave functions are expanded
24 in terms of plane waves within spheres centred on the nuclei [16]. This celebrated muffin-tin
25 model involves complex calculations the results of which were not easy to interpret (see [17-
26 18]).

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28 At the end of the thirties, just before the Second World War broke out, discussions
29 about magnetism at an international conference in Strasbourg simply questioned the
30 possibility that d electrons could form bands at all [19-20].

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3. The Sixties; the time of Jacques Friedel and his d band model

After the War, matters settled down, and in 1964, in his Institute of Metals Lecture, J. Friedel
independently re-developed a tight-binding analysis of transition metals concentrating on the
 d band only, in a simpler and more precise way [21]. In this Lecture, Friedel introduced his
famous rectangular d band model: "For all reasonable forms $n_d(E)$ of the d band, one finds
much the same parabolic variation as when $n_d = \text{const.}$ " He then provided the reader with an

equation which does give the parabolic variation of the atomic cohesive energy (with respect to isolated, free atoms, the sublimation energy) with the number of d electrons per atom. (The direct proportionality to the electronic hopping integral between first neighbours β was also clear but the proportionality to the square root of the coordination number of the structure, obviously a secondary point at that time, was missed in the equation simply because the width of the d band was taken as $2|\beta|$, instead of $\sqrt{12}z_c|\beta|$ as it should be for the rectangular d -band where z_c is the coordination number: the number of nearest neighbours per atom. Note that for the real d -band, the width is of the order of $2z_c|\beta|$. For the Gaussian d -band, the width (support) is infinite and one defines instead the standard deviation $\sigma = \sqrt{\text{var}} = \sqrt{\mu_2}$ which equals $\sqrt{z_c}|\beta|$. See Appendix A).

Françoise Cyrot, *née* Lackmann, substantiated her thesis director's assertion about "all reasonable forms $n_d(E)$ " in her PhD thesis (and in [22], in French). For that, she developed the integrals $n_d(E_F) [= \int^{E_F} n_d(E)dE]$ and $E_B(E_F) [= \int^{E_F} E n_d(E)dE]$ for various forms of $n_d(E)$ and numerically plotted the latter versus the former. (Only for the rectangular model can one directly get an analytical formula showing a strict, shifted, parabolic dependence $a[n_d(E_F)-5]^2$.) She used the mathematical formalism of moments (see Appendix A) to approximate the density of states (DOS) of the electrons in transition metals for two reasons: (i) it had already been used to approximate the DOS of the lattice vibrations by Montroll in 1942/3 [23], (ii) in the case of the frequency distribution of the normal states of a Hamiltonian describing a set of discrete atoms containing some degree of disorder, so that the cyclic boundary conditions are no more useful, physicists have found a way to calculate the moments by computing closed graphs, which one can also nicely visualize as closed walks, on the lattice. This was first found (published) by Pirenne in 1958 [24], and, independently at about the same time, by Domb, Maradudin, Montroll and Weiss in 1959 [25], for the study of vibrations on disordered systems (viz. crystals containing isotopes randomly distributed, or mixed binary alloys). In the case of Domb et al., the harmonic interactions were limited to first neighbour interactions (as it is the case in tight binding) and they could develop more applicable relations than Pirenne's general formulae. Thus this naturally was a method of choice for Fr. Cyrot-Lackmann (and Friedel) as she wanted to study the cohesion of liquid transition metals (after discussions with Loup Verlet who was working in the nearest neighbour university building in Orsay) [26]. It was also well suited to calculate surface tensions as there are simply fewer closed graphs related to surface atoms than to bulk atoms.

4. The Seventies (1970) and early Eighties; François Ducastelle and the second moment interaction model

After computing the cohesive energy of a solid, the next idea naturally was to investigate its elastic properties. It was however rapidly realized that the simple rigid band model could not reproduce the bulk modulus (the lower the first nearest neighbour distance, the larger the β overlap interaction, thus the larger the band and the larger the cohesive energy.) [27-28]. It was not possible to go further in a simple way with this band model in order to reproduce even just the main features of the experimental data collected by Gschneider Jr. for the equilibrium atomic volumes, the bulk moduli and the shear moduli which also exhibit parabolic shapes for the transition metal series, at least for the $4d$ and $5d$ series (Gschneider's figures 11, 6 and 3 respectively in his 1964 review paper [29]. The $3d$ series is complicated by magnetism). François Ducastelle, Françoise Cyrot-Lackmann's thesis student, was the first to take this problem over by adding to the purely binding band contribution (purely binding in the simple model adopted) a purely repulsive contribution as a simple sum of repulsive pairwise interactions which he took of the Born-Mayer, $\exp(-pR)$, form, a form particularly suited to the exponential R -form (see Appendix C) of the overlapping integral β chosen by Friedel at interatomic distances in the equilibrium condensed state (on the account that "their [small] number of spherical [nodes] allows them [the atomic d -orbitals] to decrease exponentially as $\exp(-qR)$ at [relatively short] distance from the origin" [30]). With respect to the usual all-pairwise potentials (e.g. Born, Lennard-Jones) it was important to clearly emphasize that the band binding contribution " E_B ne peut pas s'écrire comme une somme de contributions de paires d'atomes bien que μ_2 s'obtienne de cette façon, ceci parce que E_B est proportionnel à $\sqrt{\mu_2}$ et non à μ_2 ." [31]. With this natural and consistent choice of exponential functions, François Ducastelle could develop some relatively simple formulae for the equilibrium parameter, the total cohesive energy at equilibrium, the bulk modulus, and the cubic elastic shear moduli for various elementary atomic structures. For the fcc case for instance, he obtained c_{44} and c' both proportional to $1-2q/p$. François also obtained $c_{44}/c_{12}=(1-2q/p)/(1-2q/3p)$, and, in order to get a good agreement with experimental data, he indicated that p should be comprised between $3q$ and $5q$. Thus, François Ducastelle could reproduce rather well, at least for the fcc transition metals, the non negligible departures from the Cauchy relationship for the cubic structures ($c_{12}=c_{44}$, not to be confused with the $c'=c_{44}$ isotropic relationship), a feature that a pairwise potential could absolutely not reproduce,

whatever its parameterisation (for some comments on the Poisson-Cauchy relations, see Appendix D).

After reproducing the structural and cohesive properties of a solid at, and around its equilibrium state, the following step was to look after the properties of structural defects such as surfaces and vacancies (to start with): their energies of formation and their relaxed atomic structures. For instance it was known that the classical (non oscillatory) all-pairwise atomic potentials give a vacancy energy formation equals to the cohesive energy per atom, which contradicts experimental data for metals by a factor of about three to four, and that they predict an outward relaxation for surfaces when an inward relaxation is usually measured (much less was known about the atomic relaxations around a vacancy). The conceptual difficulty was, however, to go beyond the paradigm of periodicity, so connected to the paradigm of reciprocal space. It is easy to realize, afterwards, that the tight binding and moment approach is actually made for that. It proved difficult to realize it spontaneously at that time and this only came slowly. One had to be sure that no hypothesis or condition was violated, notably self-consistency.

In the manuscript of his thesis, Fr. Ducastelle showed that, because the number of d electrons per atom in the solid does not change under a small elastic transformation, the formula $E_B = -\text{const} \cdot \beta_o \sqrt{\sum_j e^{-2qR_j}}$ is valid for any filling of the d band. In his article, however, he just wrote 'il est facile de voir' and did not even give that formula which, obviously for us now, can be re-written as $E_B = -\text{const} \cdot \beta_o e^{-qR} \sqrt{z_c}$ for a perfect, or only elastically deformed, crystalline structure, and to $E_B(i) = -\text{const} \cdot \beta_o e^{-qR} \sqrt{z_c(i)}$ for every atom i in a complex structural defect provided electrical neutrality is maintained at first order of approximation for each atom, which is true in metals thanks to metallic screening. It was simply beyond preoccupations in 1970, and even in the simple case of perfect crystal, the (already solved) problem was raised eighteen years later by Ackland, Finnis and Vitek about the Gaussian formulation [32]. The choice of a Gaussian $n_d(E)$, instead of the rectangular function originally used by Friedel in 1964, actually rendered the 'il est facile de voir' less straightforward than in the rectangular case where $E_B = -[(n_d^2 - 10n_d)/20] \cdot |\beta| \sqrt{z_c}$ which obviously gives $E_B = -\text{const} \cdot |\beta| \sqrt{z_c}$ if n_d remains constant per atom (see Appendix A). The choice of a Gaussian $n_d(E)$ came from the fact that it is the first level of the Edgeworth series which can naturally include higher order moments [22]. Within the second moment approximation, Ackland et al. [32] provided a mathematical demonstration of the validity of

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3 the proportionality to $\sqrt{\mu_2(i)}$, and thus to $\sqrt{z_c(i)}$, in any local environment which preserves
4 the local charge neutrality and the original symmetry of the local DOS (only compression or
5 stretching by a constant factor, plus global shift to maintain charge neutrality).
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9 Considering electrical neutrality at the atomic level even around a vacancy also means
10 neglecting the Friedel charge oscillations, which is entirely valid if one is not trying to analyse
11 them, as we now know for sure. Might have it represented a conceptual difficulty for the
12 students of Friedel in spite of Friedel's own pragmatism? It simply was not that obvious, and,
13 whereas some people made it right in the details of their calculations, some people made it
14 wrong. Sutton et al.'s article, with a first principles background, masterly settled the point in
15 1988 [33].
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19 Yet, in 1976, Allan & Lannoo had already considered these problems, in an article
20 which contains a discussion of the influence of self-consistency on the relaxation near a
21 vacancy in transition metals [34]. They had also obtained a very simple formula for the fcc
22 vacancy formation energy: $E_{\text{vac}} \sim E_{\text{coh}} \cdot (1-2q/p)/(2[1-q/p])$ (to first order in $1/z_c=1/12$). E_{coh} is
23 the corresponding cohesive energy, with respect to neutral free atoms), which gives a ratio
24 $E_{\text{vac}}/E_{\text{coh}}$ comprised between 0.25 and 0.375 for $3q \leq p \leq 5q$, which sensibly agrees with
25 experimental values (first nearest neighbour pair potentials give $E_{\text{vac}} = E_{\text{coh}}$).
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29 Allan and Lannoo [34-36], Gordon, Cyrot-Lackmann and Desjonquères [37], Masuda
30 and Sato [38], Gupta [39], Desjonquères and Spanjaard [40-41], Tomanek and Bennemann
31 [42]: They all used Ducastelle's model to investigate more or less complex systems, including
32 adatoms, small clusters, screw dislocation, carrying out some more or less extended relaxation
33 on the atomic positions near the defect, always trying to keep closed form analytical formulae
34 as much as possible. When it was not possible, as in the case of the screw dislocation in dilute
35 bcc transition metal alloys, Masuda and Sato had everything to "calculate the total energy as a
36 function of the atomic displacements" and "the atoms in the crystallite [were] relaxed along
37 the screw dislocation." [38]
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51 **5. 1984; the Finnis-Sinclair article**

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53 So what was new with Finnis and Sinclair 1984 [43], who acknowledged they chose " $f(\rho)$ to
54 be $\sqrt{\rho}$, so as to mimic the result of tight-binding theory"? I see several important points (from
55 a to f):
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59 a . The title: "A simple empirical N-body potential for transition metals." By contrast with
60 previously mentioned articles, they do not announce the calculation of a specific property but

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3 they present a tool.

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5 *b.* Their pragmatism: “the present approach is empirical”, “the consequences of the form of
6 the model (...) do not depend on the physical interpretation.” One may compare this attitude
7 with Newton’s “hypotheses non fingo.” Pragmatism also includes some amount of anti-
8 Cartesianism.
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11 *c.* A general program: “for the purpose of atomistic simulation”, with explicit consideration
12 for forces at the atomic level: “In order to perform atomistic simulations of crystals containing
13 defects it is essential to have a rapid algorithm for calculating the force on each atom.” They
14 do provide the reader with general analytical formulae for calculation of forces. This will
15 allow for Molecular Dynamics, not just static minimization. (On MD simulations using *n*-
16 body potentials, see Appendix E.)
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19 *d.* The Zeitgeist: Daw and Baskes had just published their two articles [44-45]. So it was in
20 the air. In an interview in August 2000, Michele Parrinello declared that in 1983 “we invented
21 what is called the glue potential, on which Ercolessi wrote his thesis. He was drafted for
22 military service, and the work was stopped for a year and a half. During that time other people
23 had similar ideas, and applied them in metals. So due to the draft we lost time, and bit of
24 priority on this problem, but that’s life.” [46]
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33 Yet there are obvious philosophical differences between these three approaches:

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35 *(i)* Ercolessi, Parrinello and Tosatti declared that “although further theoretical justifications of
36 this scheme can be found in the so-called embedded-atom method,” they did “not believe that
37 a truly first principles derivation can be given” [47] and they worked out purely empirically
38 constructed analytical functions, carried out once, for gold [48].
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42 *(ii)* Daw and Baskes used purely numerical functions deduced from first principle calculation
43 or via a semi-empirical approach. These functions can only be tabulated and plotted.
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47 *(iii)* Finnis and Sinclair used simple analytical functions, with the square root embedding
48 function, “so as to mimic the result of tight-binding theory.”
49

50 The origin of Daw and Baskes Embedded Atom Method has later been traced back,
51 probably by Foiles [49-50], to Friedel 1952 impurity-in-jellium model [51] (see Appendix F).
52 The basic idea from which Daw and Baskes drew on is that an atom in a metallic environment
53 does not feel the detailed structure of the nearby atoms due to the effective screening in
54 metallic systems. Each atom is considered as hosted in a homogeneous gas (LDA spirit) and
55 its energy becomes a functional of the local host electron density in which it is immersed.
56 With this approach which only considers the local electronic density, it is difficult to
57 distinguish between fcc and hcp structures for instance. A pragmatic way to go is to consider
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3 under the embedding function, square root or whatever, sums of pairwise interactions which
4 include the third neighbours. By contrast, interpreting the square root as a signature of second
5 moment approximation allows one to see a more sophisticated way to go further in principle,
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7 by trying to include more moments in the formalism.
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10 *e.* Given the pragmatism of the Finnis-Sinclair approach, and the similarity with the
11 embedded atom method, the FS approach was soon extended to noble metals [52] (In 1976,
12 Allan and Lannoo had already noted that the Ducastelle model works pretty well for noble
13 metals [34]).
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17 *f.* The fast increase of computer power allowed for the fulfilling of the program about
18 “atomistic simulation” in the following years (see Appendix E).
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22 23 **6. Short conclusion; for a continuing story**

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25 The way from the perfect crystal and the so useful and wonderful reciprocal space
26 (experimentally accessible for almost a century thanks to X-rays for instance) to the real space
27 and the defects at the atomic level proved to be a long path which demanded several moments
28 of reflexions. It is clear that there is still place for continued action, on an at least bimodal
29 way based on theory and on practice, as this special issue shows it.
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39 I thank Professor Jacques Friedel, as well as François Ducastelle, for many invaluable
40 discussions, by post mail and email. I also wish to thank the library department of the École
41 Polytechnique for providing me with many ancient articles and books.
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46 **Appendix A: the origins of the moments and the method of moments**

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48 A known positive function (reasonably well behaved, e.g. a weight function, a probability
49 distribution function) can be geometrically described (analysed) through its moments (which
50 are usually normed and centred, but attention must be paid if a more general formalism is
51 adopted). The zeroth order one corresponds to its surface (its mass, usually normed to 1), the
52 first order moment gives the centre (centre of mass, the mean value of the weighted X -line),
53 with the second order moment one can get a measure of the ‘width’ of the function (the root
54 mean square deviation with respect to the chosen origin, directly the standard deviation if it is
55 with respect to the centre of the function), with the third order moment combined with the
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previous one one can get a measure of the asymmetry of the function, and with the fourth order moment one can have some indication on the mono or bimodality of the function.

If one does not know the function by itself, but can have access to its first moments (one way or another), one then has methods to approximate that function although the approximation is not unique and may not be too good if one is after a precise description of the function (this is usually not the case at the beginning of a new field of research, as with Friedel in the 60s, but it rapidly turned out to be in the 80s). The expression of a distribution as a function of its moments does not constitute a converging series at all. When the number of moments gets large, an elegant solution to that so-called moment problem is based on the continued fraction technique. This is a mathematical problem which goes back to I.J. Bienaymé (1852) and P.L. Čebyšev who is the founder of the use of continued fractions for the method of moments (Tchebychef 1874, his disciple Markov in 1884, and Stieltjes, independently, in 1894). The solution is also closed to the recursive method (Lanczos' method, see [3-4], and all contributions by Heine, Haydock, etc., in [53]). For the historical connection between continued fractions and Padé approximants, see [54].

The 'second moment' is the second order moment, thus the third moment. As usual, beware of notations and conventions, normalisation (yes or not, per atom, or even per electronic state if they are all equivalent.) and choice of origin (e.g. centred or not).

With the following notation, $m_n = \int X^n f(X)dX$; $\alpha_n = \frac{1}{m_0} \int X^n f(X)dX = \overline{X^n}$ and $\mu_n = \frac{1}{m_0} \int (X - \alpha_1)^n f(X)dX = \overline{x^n}$ with the centred variable $x = X - \alpha_1$, I simply recall the following classical results (e.g. see [55]):

$\mu_0 = 1$	$\mu_1 = 0$	$\mu_2 = \overline{x^2}$	$\mu_3 = \overline{x^3}$	$\mu_n = \overline{x^n}$
$\alpha_0 = 1$	$\alpha_1 = \overline{X}$	$\alpha_2 = \mu_2 + \alpha_1^2 = \mu_2 + \overline{X}^2$	$\alpha_3 = \mu_3 + 3\alpha_1\mu_2 + \alpha_1^3$	α_n
$m_0 = S$	$m_1 = S\alpha_1$	$m_2 = S\alpha_2$	$m_3 = S\alpha_3$	$m_n = S\alpha_n$

From the notation $\mu_2 : \sigma^2$, one gets $\sigma^2 = \alpha_2 - \alpha_1^2 = \overline{X^2} - \overline{X}^2$.

When the distribution is known, the μ_n , because they are centred, are the easiest moments to calculate.

The second moment approximation does not mean that there is a series which is truncated to its second moment (or third term). It means that no other parameter is available.

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3 Yet, with only three moments, the distribution can be rectangular, Gaussian, parabolic, ... For
4 instance let us consider a rectangular distribution of surface S , of width w and centred on M ,
5 and a Gaussian (Laplace-Gauss) distribution of surface S , of half 'width' σ at $1/\sqrt{e}$ height and
6 centred on M . These two distributions being symmetric with respect to their centres M , their
7 odd centred moments are null. Their even moments μ_{2n} are $w^{2n}/[(2n+1)2^{2n}]$ for the rectangular
8 distribution, and $\sigma^{2n}(2n)!/(2^n n!)$ for the Gaussian distribution. Thus nothing more than three
9 parameters, S , M and w , or S , M and σ , are required to entirely describe these two
10 distributions and their moments. Conversely, three parameters, m_0 , m_1 (or α_1) and m_2 (or α_2)
11 or μ_2) can define a rectangular or a Gaussian distribution. These two distributions obviously
12 have different shapes (and different moments beyond μ_2 , e.g. μ_4 equals $144\mu_2^2/90$ for the
13 rectangular case, and $3\mu_2^2$ in the Gaussian case).

14 For an elementary crystal which can be described by a tight-binding Hamiltonian, one
15 considers that every atom has m_0 equivalent electronic state available (10 for the d states, spin
16 state included), and the {Pirenne—Domb et alii—Cyrot-Lackmann}-theorem gives $\alpha_1 = E_0$,
17 the inner atomic level which is equal to the atomic level E_{at} plus a shift α due to the fact that
18 the atoms are not isolated, and $\mu_2 = z_c \beta^2$ (there are z_c closed walks which go to a first
19 neighbour and thus contribute, way and return, $\beta \cdot \beta$). Assuming a rectangular distribution, one
20 thus gets $w^2/12 = z_c \beta^2$ hence $w = \sqrt{12} \sqrt{z_c} |\beta|$ whereas $n_d(E_F) = \int_{E_0-w/2}^{E_F} A dE = \frac{10}{w} [e_F + w/2]$ (since
21 $S = Aw = m_0 = 10$ and noting e the centred variable $e = E - E_0$) and
22 $E_B = \int_{E_0-w/2}^{E_F} (E - E_{at}) A dE \sim \frac{10}{2w} [e_F^2 - (w/2)^2]$ if one neglects the shift α for the sake of clarity,
23 which gives, after some simple algebraic manipulations, $E_B = -2.5w + \frac{w}{20} [n_d(E_F) - 5]^2$, a
24 shifted parabola in $n_d(E_F)$, and also a linear function in w , hence $E_B = -\text{const} \cdot |\beta| \sqrt{z_c}$. Assuming
25 a Gaussian distribution does not alter the conclusions but makes the demonstration purely
26 numerical for the parabolic shape, and more subtle (at least to my taste) for the linear
27 dependence in $|\beta| \sqrt{z_c}$. In his truly remarkable sometimes intuitive way, Friedel 'knew' in
28 1964 that these results would not depend much on the shape of $n_d(E)$. Yet, as far as I am
29 concerned, I can understand it only through the demonstrative work carried out by Fr. Cyrot-
30 Lackmann.

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Note on the bimodality indicator

Jean-Pierre Gaspard [3-4] noticed that the ratio $\tilde{b} = (\mu_4\mu_2 - \mu_3^2 - \mu_2^3)/\mu_2^3$, which can be deduced from the first two terms of the continued fraction of the resolvent of the distribution function, gives some indication on the mono or bimodality of a distribution. A distribution with $\tilde{b} \gg 1$ is monomodal whereas a distribution with $\tilde{b} \ll 1$ is bimodal. It is tempting to propose a critical value for \tilde{b} . However such a critical value does not exist in a universal way. Just to give two examples, it is 0.8 for the symmetrical beta law $([x(1-x)]^{a-1})$, for $0 \leq x \leq 1$, a being a real number > 0) but for the symmetrical mixture of two equivalent Gaussians differing only by their centres, it is 1.5. The case of a non symmetrical distribution will be more difficult to decide. Let us also note that, using Pearson's coefficients $\beta_1 = \mu_3^2/\mu_2^3$ and $\beta_2 = \mu_4/\mu_2^2$, one has $\tilde{b} = \beta_2 - \beta_1 - 1$.

Some original quotations which introduced the moments:

Marin Mersenne (French monk and universal scientist, well known for being in touch with almost all savants of his time), in his free translation/adaptation in 1634 of the not yet published lectures of Galileo Galilei on Mechanics at the University of Padua in the 1590s: "Le *moment* est l'inclination du mefme corps, lors qu'elle n'est pas feulement confidérée dans ledit corps, mais conioinctement avec la fituation qu'il a fur le bras d'un leuier, ou d'une balance." [56]

Galileo Galilei, in *Le Mecaniche*, posthumously published in Ravenna in 1649: "Momento è la propensione di andare al basso, cagionata non tanto dalla gravità del mobile, quanto dalla disposizione che abbino tra di loro diversi corpi gravi" [57]

Irénée-Jules Bienaymé (1852): "(...) si l'on appelle μ_Σ la moyenne des puissances Σ de toutes les erreurs possibles, on aura $\int \varepsilon^\Sigma d\varepsilon \varphi(\varepsilon) = \mu_\Sigma$ " [58]

Pafnouty Lvovitch Tchebychev (1874): "En cherchant à tirer tout le parti possible sur les valeurs limites de l'intégrale $\int_a^h f(x)dx$ des valeurs des intégrales $\int_A^B f(x)dx$, $\int_A^B xf(x)dx$, $\int_A^B x^2 f(x)dx$, $\int_A^B x^m f(x)dx$, où l'on a $A < a$, $B > b$, et où $f(x)$ reste positive, je suis parvenu à

reconnaître que ces recherches conduisent à des théorèmes d'un nouveau genre, concernant le développement de l'expression $\int_A^B \frac{f(x)}{z-x} dx$ en fraction continue, qui joue un si grand rôle dans la théorie des séries." [59]

Thomas-Jan Stieltjes (1894): "Considérons sur une droite infinie une distribution de masse (positive), la masse m_i se trouvant concentrée à la distance ξ_i de l'origine. La somme $\sum m_i \xi_i^k$ peut être appelée le *moment* d'ordre k de la masse par rapport à l'origine." [60]

Appendix B: on Tight Binding and LCAO

Felix Bloch demonstrated (in much more details than some forerunners as Houston, Strutt, Frenkel, and quite independently) that if the ionised atoms are positioned regularly, as in a crystal, then, for the electrons in such a periodic lattice, there are solutions of Schrödinger's equation in the form of plane waves that describe electrons travelling in any direction through the crystal without being scattered [61]. The Bloch plane-wave solutions are more complicated than the de Broglie wave of an electron in free space, but a wave-vector \mathbf{k} may still be defined: one has to deal with de Broglie waves, "die im Rhythmus des Gitteraufbaus moduliert sind." Exact solutions for any particular choice of the periodic potential $V(\mathbf{r})$ (: the interaction potential between the conduction electrons and the lattice) are probably impossible to find and Bloch worked out exact solutions in a limit case he knew from his time in Zürich where he, and Heitler and London enjoyed walking together. F. Bloch drew on the idea that Heitler and London had used on their treatment of the hydrogen molecule, that of constructing electron wave functions starting from a basis of unperturbed single-atom ground-state orbitals. F. Bloch called it the limit case of stark gebundener Elektronen (strongly bound electrons), which came to be known as tight-binding approximation. In his 1931 article, Erich Hückel extensively referenced F. Bloch [62]. At the request of their common director Heisenberg, Peierls, among many other things, worked out the solution for a nearly free version of $V(\mathbf{r})$, instead of the tight-binding version chosen by Bloch, and was delighted to get

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3 some similar results which were thus likely to be independent on the details of the interactions
4 of the electrons with the atoms. A.H. Wilson developed the band theory further (see [63-65]).
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7 Wigner and his student Seitz blurred the landscape in 1933 when they explicitly
8 considered the work of Bloch as mainly based on the hypothesis of free electrons in chemistry
9 [9]. Mott and Jones coined the English expression ‘tight binding’ approximation in their 1936
10 book [12]. Friedel and his co-workers always quoted Hückel for the tight-binding
11 approximation.
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15 Yet, in 1931, referring to F. Bloch 1928, Erich Hückel wrote: “Es lassen sich dann die
16 Eigenfunktionen eines Elektrons durch Linearkombinationen der Eigenfunktionen des
17 Elektrons bei getrennten Atomen annähern.” (p. 219 of [62]). And, in 1955, Reitz clearly
18 wrote: “the *linear combination of atomic orbitals*, or *Bloch*, or *tight binding method*. This
19 technique was first proposed for solids by Bloch.” (page 16 of [66])
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25 It must be recognized that Bloch’s name, because of Bloch’s theorem, conveys the idea
26 of periodicity, and Fourier transforms. By contrast, because Hückel dealt with finite size
27 molecules, his name conveys the idea of as distorted as you like configurations with a real
28 space approach (even if Hückel happened to also use Bloch’s periodicity trick because he
29 actually dealt with benzene, a cyclic ‘aromatic’ molecule!). It is also probably difficult to
30 comprehend that some electrons may be delocalized without being totally free. The most
31 relevant picture here is that of itinerant electrons, hopping from one atom to the next, but not
32 necessarily forming a homogeneous jellium between the atoms as free electrons do.
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40 Lennard-Jones is usually given as the founder of the LCAO method in 1929 [67]
41 although this was the way of doing at that time: Hund 1927 onward, Mulliken 1928, Lennard-
42 Jones 1929. Mulliken formalized the technique and introduced the English term ‘LCAO’ in
43 1935 [68].
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47 There is a difference in spirit between Heitler and London 1927 and the so-called Hund-
48 Mulliken approach, at least in their premises. Heitler & London 1927 start with atomic
49 orbitals, AOs, (e.g. $\varphi_A(\mathbf{r})$ and $\varphi_B(\mathbf{r})$) which they combine, through multiplications and
50 additions, to generate symmetrical and antisymmetrical functions. The building blocks of the
51 Hund-Mulliken approach are LCAOs, sums and differences of atomic orbitals (e.g.
52 $\varphi_A(\mathbf{r})+\varphi_B(\mathbf{r})$ and $\varphi_A(\mathbf{r})-\varphi_B(\mathbf{r})$) which are then combined to generate symmetrical and
53 antisymmetrical functions. These building blocks are more appropriate when the atoms are
54 relatively close together, yet still retaining some of their atomic character: this is the spirit of
55 the ‘tight binding’ approach.
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Tight binding has also been successfully developed for covalent materials by Friedel, Leman, Lannoo, Allan, Gaspard, and others with the use of moments. We are dealing here with s and p electronic states, which are quite different in nature from the atomic like d states. But because of the sp^3 hybridization, these materials crystallize in the cubic diamond atomic structure, which is an open structure so that the influence of the second neighbours can be neglected in a first approximation with respect to the influence of the first neighbours. A tight binding treatment is relevant, and successful. The electrons are nevertheless free to move from one atom to any other through the covalent bounds and the $E(k)$ dispersion for silicon is very close to the free electron dispersion at small k . The cubic diamond materials have been the first for which n -body potentials have been developed [69], although for a completely different reason. The tetrahedral angles between the sp^3 bonds is a fundamental of the cubic diamond structure and can only be reproduced with three body terms with explicit angular dependence (and it takes three points to define an angle). The Cauchy relations are violated for cubic diamond materials for two reasons: the interactions are not pairwise and the atoms are not centres of symmetry. The Cauchy discrepancy being negative, an embedded function of the usual type cannot be expected to work. The presence of explicit angular dependent terms seems necessary.

Appendix C: exponential or power laws?

The exponential form of the overlap, or transfer or hopping or bond, integral, has been chosen historically, in part because of the widespread use of the “Slater” orbitals [70]. Ab initio calculations that the dependence should rather be of the inverse power form [71-72].

In the immediate vicinity of the equilibrium first neighbour distance R_o , it does not matter since one has $e^{-\kappa R} \sim cR^{-n}$ with $n = \kappa R_o$ and $c = (R_o/e)^n$. If one wants to stretch the bonds further, i.e. to extend the validity of the overlap law, both solutions fail and pragmatism must prevail, especially for the smoothing of the function down to zero (e.g. see §7.3.2 of [8]).

Appendix D: on the Cauchy relations

Following the mechanical school of Navier, Poisson, Cauchy, Clausius and Saint-Venant, one should have special relations between elastic constants which A.E.H. Love called Cauchy relations in the historical introduction of his famous treatise on elasticity more than a century ago [73]. These relations are consequences of the hypothesis of interactions between atomic point centres, together with other hypotheses such as pairwise interactions, atoms being symmetry centres of the structure, and no constraints at zero deformation. They proved to be incompatible with experimental measurements (once properly made..., for instance by W. Voigt) so that the atomic hypothesis was contested by positivist anti atomists such as Pierre Duhem, by no means an obscurantist. He was right in the sense that the real atoms are not point centres with no internal structure. From an opposite point of view, in the sixth volume of the Handbuch der Physik series in 1928, J.W. Geckeler wrote that for the elementary metals which violate the Cauchy relations, one must conclude that their atomic structure is not just a simple (Bravais) lattice. Still later on, Raman and his disciples in India, and Laval in France were to oppose Born about the number of independent elastic constants for diamond.

Cauchy's name is also associated to the opposite mechanical school, viz. the continuous mechanics tradition. The appellation Poisson-Cauchy relations would be more fitted, from an historical point of view.

Daw and Baskes noted that the positive curvature of the embedding function implies positive Cauchy discrepancies. Finnis and Sinclair reproduced the same remark, noting that it is the case for the square root function. Thus for metals with negative discrepancies, such as rhodium and iridium, it means that these metals have some basic properties which are not taken into account by the EAM model, for instance explicit angular dependant terms (hence the MEAMs: modified EAMs).

DFT ab initio calculations, in full electrons or with pseudopotentials, only started in the eighties, with sometimes only a moderate success as far as the calculation of elastic constants is concerned (see [1]).

Appendix E: the first MD simulations with n-body potentials

As far as I know, the first MD simulation with a metallic n-body potential was carried out by S.M. Foiles in 1985 with an EAM potential for liquid transition and noble fcc metals (Ni, Pd, Pt, Cu, Ag, and Au) [74].

It is worth noting that at the same time, Stillinger and Weber designed an n-body potential for silicon, with explicit angular dependence, based on experimental and ab initio data, and also performed Molecular Dynamics calculations to check the liquid state [75].

Ercolessi, Parrinello and Tosatti in 1988 (published) performed MD simulations with their glue gold model in order to check the melting temperature of their model [52].

Rosato, Guillope and Legrand in 1989 are the first who carried out MD simulations with FS-like potentials, with Ducastelle's exponential functions, on fcc transition metals [76].

For sake of completeness, I also mention the MD simulations of systems of rigid molecules: When atoms of rigid molecules interact together through relatively long ranged Van der Waals interactions, one can say that the molecules, which are the elementary (rigid) bodies of the system, interact together through n-body potentials. The first MD simulation of this kind is by Barojas, Levesque and Quentrec in 1973 [77]. The interaction model was described in 1967 by Sweet and Steele [78].

For a short introduction to atomistic simulations, Monte Carlo Metropolis and Molecular Dynamics, with some historical information, see [79].

Appendix F: on the origins of the EAM

Stephen Foiles wrote in 1996 ([50], + see [49]) that "the idea of an embedding energy was first suggested by Friedel [51] and later developed further by Nørskov and Lang [effective medium theory 1980] and by Stott and Zaremba [quasi-atom concept 1980]."

In the late 40s, J. Friedel carried out the first numerical study of grain boundaries at the atomistic level (see [80]). Yet, a little disappointed by the crudeness of the pairwise interatomic potentials he had had to use, he decided to learn more about electronic interactions in metals and was introduced by his cousin Ch. Crussard to N.F. Mott in Bristol. There he also met Charles Frank, and his future wife.

In 1936, Mott, concerned with dilute solid solutions (metallic alloys, Hume-Rothery

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3 electron concentration rule (the famous 21/13 ratio, in 1926), influence on electric resistivity)
4 had considered the problem of local screening of charges around (highly dispersed) impurities
5 in a metallic matrix, notably when the dissolved and solvent metals do not occupy the same
6 column in the periodic table, e.g. when an atom of zinc or aluminium is dissolved in copper.
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11 “The extra electrons of the dissolved atom must be regarded as belonging to the lattice rather
12 than to the atom. We should therefore expect the dissolved atom to carry an extra positive
13 charge z , equal to 1 for zinc, 2 for aluminium” [81]. Friedel ([51, 82]) modified Mott’s rapidly
14 decaying solution (à la Debye-Hückel) into a less rapidly decaying solution with oscillations
15 which later came to be known as ‘Friedel oscillations’.

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19 The conceptual difficulty master was to consider the extra electrons of the impurity as
20 given to the lattice, thus unbound, and yet to have the jellium respond as a local charge
21 concentration (electron polarization cloud). One indeed finds in Friedel 1952 the idea that “an
22 impurity atom is embedded in a regular lattice”, and that the perturbation is only local (then,
23 self consistently, that embedded atom can only depend on its local environment).

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28 It must however be recognized that the lack of simple guidelines, except complex ab
29 initio calculations or optimization fitting on empirical data, is not in the spirit of J. Friedel’s
30 approach.
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41 **Appendix G: unabridged references**

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On the origins of the Finnis-Sinclair potentials

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Contents:

1. Introduction

2. The Thirties; first steps, nullified by sensible hesitations

3. The Sixties; the time of Jacques Friedel and his d band model

4. The Seventies (1970) and early Eighties; François Ducastelle and his followers

5. 1984; the Finnis-Sinclair article

6. Short conclusion; for a continuing story

Acknowledgments

Appendix A: the origins of the moments and the method of moments

Appendix B: on Tight Binding and LCAO

Appendix C: exponential or power laws?

Appendix D: on the Cauchy relations

Appendix E: the first MD simulations with n-body potentials

Appendix F: on the origins of the EAM

Appendix G: unabridged references

1
2
3 Dear Professor Bristowe,

4
5 I thank you for your positive comment about my article.

6
7 I just took some vacations and that is why I am answering so late.

8
9
10
11 It is of course always difficult to translate texts which are some times very old (old French for
12 Mersenne, old Italian for Galilei). Here are my tentative translations. Let me know if they are
13 understandable (I hope I do not use false friends). Feel free to modify accordingly. Thanks.

14
15
16
17 In the attached FSOrgins_OHD-3.doc Word document, I embedded these translations in
18 parentheses. (foot notes are not customary in Phil. Mag. Another appendix within the
19 appendices would be cumbersome.)

20
21
22
23 “ E_B ne peut pas s’écrire comme une somme de contributions de paires d’atomes bien que μ_2
24 s’obtienne de cette façon, ceci parce que E_B est proportionnel à $\sqrt{\mu_2}$ et non à μ_2 .”

25
26 “ E_B cannot be written as a sum of atomic pair contributions although it is the case for μ_2 ,
27 because E_B is proportional to $\sqrt{\mu_2}$, not to μ_2 .”

28
29
30 “*Le moment* est l’inclination du mefme corps, lors qu’elle n’est pas feulement confidérée dans
31 ledit corps, mais conioinctement avec la fituation qu’il a fur le bras d’un leuier, ou d’une
32 balance.” [56]

33
34
35 “*Moment* is the inclination of the same body, when it is considered not only within the body,
36 but with respect to the effect it has on the branch of a lever, or of a balance.” [56]

37
38
39 “*Momento* è la propensione di andare al basso, cagionata non tanto dalla gravità del mobile,
40 quanto dalla disposizione che abbino tra di loro diversi corpi gravi” [57]

41
42
43 “*Moment* is the propension to go down, considered not as much with respect to the weight of
44 the solid, but rather to the relative disposition of the various weighting bodies” [57]

45
46 I am asking an Italian colleague about the correctness of this translation.

47
48
49
50 “(...) si l’on appelle μ_Σ la moyenne des puissances Σ de toutes les erreurs possibles, on aura
51 $\int \varepsilon^\Sigma d\varepsilon\varphi(\varepsilon) = \mu_\Sigma$ ” [58]

52
53 “(...) if one calls μ_Σ the average of the powers Σ of all the possible errors, one will get
54 $\int \varepsilon^\Sigma d\varepsilon\varphi(\varepsilon) = \mu_\Sigma$ ” [58]

55
56
57 “En cherchant à tirer tout le parti possible sur les valeurs limites de l’intégrale $\int_a^b f(x)dx$ des

58
59
60 valeurs des intégrales $\int_A^B f(x)dx$, $\int_A^B xf(x)dx$, $\int_A^B x^2 f(x)dx$, $\int_A^B x^m f(x)dx$, où l’on a $A < a$, $B > b$,

1
2
3 et où $f(x)$ reste positive, je suis parvenu à reconnaître que ces recherches conduisent à des
4 théorèmes d'un nouveau genre, concernant le développement de l'expression $\int_A^B \frac{f(x)}{z-x} dx$ en
5 fraction continue, qui joue un si grand rôle dans la théorie des séries." [59]

6
7
8 "Trying to learn as much as possible on the limiting values of the $\int_a^b f(x)dx$ integral from the
9 values of the $\int_A^B f(x)dx$, $\int_A^B xf(x)dx$, $\int_A^B x^2 f(x)dx$, $\int_A^B x^m f(x)dx$ integrals, where $A < a$, $B > b$,
10 and where $f(x)$ remains positive, I realized that these researches lead to theorems of a new
11 kind, concerning the development of $\int_A^B \frac{f(x)}{z-x} dx$ in continued fraction, which plays such a
12 great rôle in the theory of series." [59]

13
14
15 "Considérons sur une droite infinie une distribution de masse (positive), la masse m_i se
16 trouvant concentrée à la distance ξ_i de l'origine. La somme $\sum m_i \xi_i^k$ peut être appelée le *moment*
17 d'ordre k de la masse par rapport à l'origine." [60]

18
19 "Let us consider an infinite straight line with a (positive) mass distribution, the mass m_i being
20 concentrated at a distance ξ_i from the origin. The sum $\sum m_i \xi_i^k$ may be called the *moment* of
21 order k of the mass with respect to the origin." [60]

22
23 "die im Rhythmus des Gitteraufbaus moduliert sind."

24 "which are modulated by the rhythm of the lattice structure."

25
26 "Es lassen sich dann die Eigenfunktionen eines Elektrons durch Linearkombinationen der
27 Eigenfunktionen des Elektrons bei getrennten Atomen annähern."

28 "Thus the eigenfunctions of an electron can be approximated as linear combinations of
29 eigenfunctions of atomic electrons."

30 I am asking a German colleague about the correctness of this translation.

31
32 p. 4 "For the Gaussian d-band, the width (support) is infinite ..". What is support?

33 The 'support' of a function $f(X)$ is the ensemble of X values over which $f(X)$ is finite (not
34 zero). For a Gaussian, it goes from minus infinity to plus infinity. It is not what one usually
35 calls the width of a Gaussian ($\sigma = \sqrt{\text{var}}$).

36 p. 4 "nearest neighbour building" means "neighbouring building"?

37 Yes. (but neighbouring as 'nearest neighbour', I believe, although I have to check with
38 Jacques Friedel. This is a petty detail)

39 p. 7 "made it right" means "got it right"?

40 Yes. Or "made it the right way", "made it correctly".

41 p. 10 "yes or not" means "whether or not"?

42 Yes.

43
44
45 I thank you for your help,
46 Olivier Hardouin Duparc.