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Electronic work-function calculations of polycrystalline metal surfaces revisited

Tomasz Durakiewicz,[1,*] Stanislaw Halas,[2] Al Arko,[1] John J. Joyce,[1] and Dave P. Moore[1]
[1]*Los Alamos National Laboratory, Mailstop K764, Los Alamos New Mexico 87545*
[2]*Institute of Physics, Maria Curie-Sklodowska University, 20-031 Lublin, Poland*

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A brief comparison of methods used to calculate the electronic work function of polycrystalline metal surfaces is presented. We show that the *ab initio* methods are unable to give values in acceptable agreement with experiments, whereas simple models based on the free-electron gas approach and classical electrodynamics work well, even in complicated electronic systems like transition metals, lanthanides, or actinides. This observation is made on the basis of previously published computations by the authors and new results for lanthanides and actinides. Surface valence transitions from trivalent to divalent for Sm and Tm are indicated. Heavy actinides work functions are presented. The results are compared with available experimental and theoretical values, and an attempt to address the reasons for *ab initio* failure is undertaken on the basis of a concept of quantum decoherence.

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I. INTRODUCTION

The work function (WF) is a fundamental property of a metallic surface. Not surprisingly, then, numerous attempts have been made in the last decades to calculate the values of WF and/or surface energy which agree with accepted experimental values. Let us first briefly discuss some of the most important approaches to modeling the work function done during the last 30 years.

In the fundamental paper by Lang and Kohn[1] the metal was modeled by use of a uniform background charge instead of the lattice of ions, with exchange and correlation effects included self-consistently. Relative agreement with experimental data was obtained for simple metals only (9 of 14 calculated). Mehrorta and Mahanty[2] used the hydrodynamic model of Bloch as well as the Tomas-Fermi approximation to calculate the WF for 26 metals, with very poor agreement. A purely electrostatic approach was done by Weinert and Watson[3] who used the so-called Mattheiss construct based on the overlapping spherical atomic charge-density approximation, and a chemical potential taken from literature, to calculate the WF for 30 metals for which experimental values were known (and also for H and Tc). Utreras-Diaz[4] performed WF calculations on the basis of the Thomas-Fermi-Von Weizsacker approach by solving the Euler equation for a slab geometry for jellium (five alkali metals) and pseudojellium (four metals). Satisfactory agreement was obtained using the pseudojellium model, but only for four alkali metals. Later the jellium WF was calculated as a function of electron density parameter by Perdew and Wang[5] within the local-density approximation for (i) electron-gas exchange correlation and (ii) exchange only. Their WF(r_s) function for both models peaks at $r_s=2$, while for higher densities it decreases, which is not observed in the real world and has to be considered an artifact. In the jellium stabilized by a structureless potential model, introduced by Perdew, Tran, and Smith,[6] the WF depends on the electron-density parameter r_s only. The electron-density parameter is the radius, in atomic units, of a sphere containing a single free electron [see Eq. (5)]. The WF was calculated for five monovalent metals, for seven divalent/polyvalent metals, and for H. Surface energies too small by 25% and work functions too large by approximately 15%, relative to experiment, were obtained by Shore and Rose[7] in the framework of their ''theory of an ideal metal.'' They noticed that jellium models are unable to predict the surface energy and WF of metals because jellium is not in mechanical equilibrium. Pseudojellium works better, but requires external forces to maintain equilibrium. By ''cleaving'' the electron gas the need for external forces was removed by Shore and Rose, and no parameters beyond the average electron density r_s were introduced. Numerical results for particular metals were not included in this paper, but from their Fig. 3 it may be seen that the WF's calculated for the low and medium electron density metals are approximately 0.3 eV above the experimental values. The surface energy peaks at $r_s=1.6$ a.u. and falls down for higher densities, which is an unphysical artifact of the same nature as in Ref. 5. The most complete work was done by Skriver and Rosengaard,[8] who employed the Green's-function technique based on the linear muffin-tin orbitals (LMTO) with tight-binding and atomic sphere approximations, to calculate WF's and surface energies of 42 metals. Their agreement within 15% with experimental data encouraged authors to claim that the ''*ab initio* calculations have reached a stage where they may form the most consistent basis for a physical description of surface phenomena.'' Good agreement with experimental values was actually obtained for monovalent, divalent, and trivalent nontransition metals. However, for $3d$, $4d$, and $5d$ metals, the WF's were substantially too high, with the result that overall agreement was actually among the worst discussed here. The full-potential LMTO was applied also by Methfessel[9] for WF calculations of seven-layer slabs of nine $4d$ transition metals, yielding very good agreement with experimental values. Recently, more attempts were made to derive the WF's from thin-slab or jellium slab calculation, taking into account the quantum size effects. Thin-slab calculation done by Wojciechowski[10] (for Li and Al only) shows very good agreement with experimental values, and seems to be very promising. Fall, Bingelli, and Baldereschi[11] also derived the

WF from thin-slab calculations for Al (only) but 10% too high. Numerous other attempts to calculate WF for one or two metals are not discussed here.

It was shown[12,13] on alkali and transition metals, that *ab initio* methods are unable to yield values of work function and/or surface energy in agreement with experiments. Due to these limitations, a return to classical electrodynamics was proposed by Brodie[14] and Halas and Durakiewicz[13] (HD models). In this paper, the HD (Ref. 13) and HD free-electron gas (HDFE) (this work) models are compared with ten *ab initio* models of WF calculation and are proven to give the best agreement of calculated WF values with experiment. We also present similar discussion for lanthanides and actinides, not calculated so far by HD models.

Experimental values of WF for lanthanides are limited. The most frequently cited compilation is by Michaelson[15] in which one finds, among others, WF values for eight lanthanides and Ba. Another compilation is given in a book by Kultashev and Rozkhov,[16] who give recommended WF experimental values for 12 lanthanides. Except for Yb and Pm, all our experimental WF's for the lanthanides were taken from these two sources. Malov, Onishchenko, and Mironkova[17] measured the WF's for 16 lanthanides, using the contact potential difference method (CPD) for both clean surfaces in nitrogen, as well as after 15 h exposure to air. While they claim that their values on the clean surfaces are the best obtained so far because of lack of oxidation, their values for Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu show only a minor difference between ''oxidized'' and ''unoxidized'' surfaces, and are shifted below other theoretical or measured values by approximately 0.5 eV. This indicates that their WF values are most probably biased by a systematic error of the order of 0.5 eV, and are therefore not discussed here.

A detailed theoretical study of rare-earth metals including surface energy and WF calculations was performed most recently by Aldén, Johansson, and Skriver.[18] They applied the Green's-function technique within the tight-binding linear muffin-tin orbitals method (LMTO). The calculated surface energies showed approximately 10% mean excess over experimental values. WF values, calculated for 15 lanthanide metals and Ba, were compared to six experimental values from Michaelson.[15] Sm and Tb experimental data published by Michaelson were not indicated in Ref. 18, in spite of the fact that theoretical values were given. The difference between theory in Ref. 18 and experiment[15] for these two metals were 0.47 eV (15%) and 0.29 eV (9%), respectively. Below we show that the results obtained by HDFE are in better agreement with experimental data than LMTO.

Bulk physical and electronic properties of actinides were studied theoretically most recently by *ab initio* self-consistent methods. Electron-phonon coupling was investigated by Skriver *et al.* for eight elements.[19] Thermal expansion for five actinide elements,[20] phase diagram for Np,[21] and structural properties of Pu (Ref. 22) were calculated by Söderlind's group. Atomic volumes for Fr, Ra, and six light actinides,[23] electronic and phonon properties of six phases of Pu,[24] and atomic volumes for light actinides,[25] were calculated by groups led by Vitos, Wallace, and Jones, respectively. However, no WF values were calculated in above-mentioned papers. Electronic structure and WF for the (111) and (100) surfaces of δ-Pu were calculated by Hao *et al.*[26] The same authors calculated the electronic structure and WF for γ-uranium.[27] Kollar, Vitos, and Skriver[28] calculated the surface energy and WF for Fr, Ra, and six light actinides. In this manuscript we show, among other results, that HDFE predicts WF values for light actinides similar to (within a few percent) either experiments or LMTO and FLMTO computations.

II. BRODIE'S AND HD METHODS

The ''return'' to the classical electrostatic image-potential approach to the work function was proposed by Brodie[14] as an alternative to *ab initio* methods. He expressed the work function of the polycrystalline metallic surface in terms of the atomic radius, Fermi energy, and effective mass of electron. Brodie's model, in spite of its simplicity, produced results in very good agreement with experimental data. His approach was therefore used by numerous researchers in spite of its phenomenological character.[10,29–39] Some drawbacks of Brodie's model were overcome by Halas and Durakiewicz[13] who proposed the use of the length of spontaneous polarization of the electron gas at the Fermi level to calculate the distance d at which the image force begins to act (HD). Polarization requires energy, which in the case of a gaseous plasma is derived from thermal energy $kT/2$. In the case of electron gas, the polarization energy would be derived from the kinetic energy of the outgoing electron, the maximum value of which at 0 K is, by definition, equal to the Fermi energy. The distance d may be therefore seen as the distance at which the outgoing electron loses all the kinetic energy to polarization. By analog to the plasma situation, we assume that at d the mother ion is completely screened. If screening was incomplete, our calculated WF values would have been much higher. Such significantly larger values of WF do not contribute to the work function measured by means of thermionic or field emission, and only slightly influence values obtained by Kelvin probes. Thanks to this new idea, it was possible to get rid of both the effective mass and uncertainty principle. Effective mass is not only a troublesome parameter, the value of which is directionally dependent, but also it might be used to artificially adjust the theoretical predictions to experimental results. Also, we view as a success the bypassing of the uncertainty principle, since the choice of the right form of it was not clear in Brodie's approach. The WF's in HD (Ref. 13) are calculated for 53 elements for which experimental values are known, using the formula

$$\varphi = \frac{43.46\alpha}{r_s^{3/2} E_F^{1/2}}, \tag{1}$$

where α is a parameter equal to 0.86 for alkali metals, Ca, Sr, Ba, Ra, Tl, lanthanides, and actinides, and equal to 1 for all other metals. The Fermi energy E_F may be either taken from literature (from *ab initio* methods) or calculated by a free-electron gas model:

$$E_F = \frac{h^2}{8m}\left(\frac{3}{\pi}n\right)^{2/3}, \tag{2}$$

where $n = 3/4\pi r_s^3$, or for practical calculations,

$$E_F = 50.03 r_s^{-2}, \tag{3}$$

where E_F is in eV and r_s in atomic units. The work function in the HD free-electron gas (HDFE) may now be expressed as

$$\varphi = 6.15 \alpha r_s^{-1/2}. \tag{4}$$

The density parameter in both HD and HDFE is simply calculated from bulk properties:

$$r_s = 1.3882 a_0 \left(\frac{A}{z\rho}\right)^{1/3}, \tag{5}$$

where A is atomic mass, z is valence (discussed below for lanthanides and actinides), ρ is density in g/cm^3, and a_0 is Bohr's radius in Å.

In Brodie's original work, image force is calculated with respect to an individual conducting sphere, whereas a flat surface is considered in both HD and HDFE. We submit that our assumption of a plane is of the same order of simplification as the one used by Brodie, since the real surface geometry can neither be described as an array of individual conducting spheres (Brodie actually performs calculations for a single sphere), nor as a flat surface. We point out that, to our knowledge, the classic image potential problem was never analytically solved for anything more complicated than a plane surface or set of plane surfaces, or a sphere. It has not been attempted to calculate the work done against the image force even for the case of a surface of electrically connected conducting spheres, much less the real surface.

As it was shown by Wojciechowski,[35] Brodie's method is capable of accounting for crystal-face-dependent variation of WF. Wojciechowski did also show that HD formalism does an even better job in accounting for this kind of effect.[39] For this reason, we do not intend to present the face-dependency problem in this paper.

HDFE calculations were performed for 67 metals. The advantage of HDFE over HD is that no fractional valencies and no data from *ab initio* calculations are used in HDFE. These extensions of Brodie's ideas, namely HD and HDFE, produce WF values in best agreement with experiment for a large number of metals (more than 15). Recall that most calculations can succeed for particular metals, but fail when extended to a large number.

Since E_F values for lanthanides were not available to the authors, the HDFE method was used. The choice of valence for lanthanides was performed on the basis of experimental and theoretical results. Open $4f$ shells make lanthanides unique in that the localized $4f$ orbitals do not contribute to bonding, and the chemical properties are similar among members of the group. This electronic structure makes the choice of surface valence a nontrivial task. Two $6s$ electrons are responsible for the divalent character of the gas phase, but most of lanthanides are trivalent in solid-state form. In this form there may exist differences in electronic properties between surface and bulk. From XPS spectra it was found that a surface core-level shift exists for Sm, which effect was primarily interpreted as a mixed-valence bulk property.[40] It was also proposed that samarium is trivalent in bulk and divalent at the surface.[41–43] A divalent Sm surface was observed by photoemission study performed on $\mathrm{SmSn_3}$ by the authors, based on oxygen dosing experiments. The same valence change from trivalent bulk to divalent surface was observed and theoretically supported for Tm.[43,44] Since the WF is a surface property, a valence of 2 was used here for both Sm and Tm. Pr and Nd are recognized as trivalent.[42,43,45] It should be noted, however, that much better agreement with experimental values is obtained if a divalent surface is assumed for Pr and Nd (see Table I). A divalent surface might be suggested, but due to the lack of theoretical predictions or experimental observations known to authors, both valencies are used for WF calculation for Pr and Nd in Table I. No experimental data are available for Pm so trivalent configuration was assumed for this metal. A valence of 2 for both bulk and surface is widely accepted and was used for Ba, Eu, and Yb.[18,46] Other lanthanides are assumed to be trivalent both in the bulk and at the surface. Actinide valencies were taken from Refs. 45 and 47.

III. RESULTS

Results of HD calculations for alkali and transition metals are published in Refs. 12 and 13. HDFE calculations for these metals were performed on the basis of data published there. Table I summarizes the input and output data used for HDFE calculation and comparison of WF's for lanthanides. HD and HDFE results for actinides as well as comparisons are displayed in Table II. In order to compare the accordance of modeling with the real world, a calculation of normalized deviation was performed for 12 models discussed above:

$$\sigma = \frac{1}{n}\sum_{i=1}^{n} ABS(WF_i^{\mathrm{calc}} - WF_i^{\mathrm{exp}}), \tag{6}$$

where n is the number of metals for which a WF was calculated. Experimental (accepted) values for polycrystalline surfaces were taken from Refs. 15 and 26. A mean value for different faces was taken if authors calculated each of the faces separately. The normalized deviation calculated this way does not diminish with increasing number of samples, therefore giving equal chances to all models, whatever the number of metals calculated. The absolute value of the difference is used because in some cases a portion of the calculated values is below and another portion above experimental values. As may be seen from Fig. 1, a majority of the *ab initio* models gives results worse than HD or HDFE. This trend is indicated by line A in Fig. 1.

Results of lanthanides WF's calculations by HDFE method and comparison with LMTO and experimental values are shown in Fig. 2. WF results by HDFE for Pr and Nd are indicated for divalent (solid line) and trivalent (dotted line) configurations. Grouping lanthanides according to valence may be seen in Fig. 3, where the work function, as a function of density, is shown. Pr and Nd are again indicated

TABLE I. Input and output values used in WF calculations by HDFE and results from literature. Underlined=rejected; ^{s}: surface; ^{b}: bulk, HDFE: this work; LMTO: Ref. 18.

						φ (eV)			
Element	A	ρ (g cm^{-1})	Z	r_s (a_0)	E_F (eV)	HDFE	LMTO	Expt. (Ref. 15)	Expt. (Ref. 16)
Ba	137.3	3.51	2	3.74	3.58	2.73	2.19	2.7	
La	138.9	6.70	3	2.64	7.16	3.25	3.06	3.5	2.96
Ce	140.1	6.78	3	2.64	7.17	3.24	3.26	2.9	2.97
Pr	140.9	6.77	2^s	3.03	5.45	3.04			2.96
			3^b	2.65	7.14	3.25	3.11		
Nd	144.2	7.00	2^s	3.02	5.48	3.04		3.2	3
			3^b	2.64	7.19	3.25	3.09		
Pm	145.0	6.48	3	2.71	6.80	3.21	3.09		
Sm	150.4	7.54	2^s	2.99	5.60	3.06		2.7	2.85
			3^b	2.61	7.34	3.27	3.17		
Eu	152.0	5.26	$\overline{2}$	3.38	4.38	2.87	2.35	2.5	
Gd	157.3	7.89	3	2.61	7.34	3.27	3.22	3.1	3.17
Tb	158.9	8.27	3	2.58	7.53	3.29	3.29	3.0	3.15
Dy	162.5	8.54	3	2.57	7.58	3.30	3.31		3.25
Ho	164.9	8.80	3	2.56	7.65	3.30	3.37		3.22
Er	167.3	9.05	3	2.55	7.72	3.31	3.41		3.25
Tm	168.9	9.33	2^s	2.89	5.98	3.11			3.1
			3^b	2.53	7.83	3.32	3.46		
Yb	173.0	6.98	$\overline{2}$	3.21	4.85	2.95	2.51		
Lu	174.9	9.84	3	2.51	7.93	3.33	3.53	3.3	3.25

in both the surface valence (divalent) region and the trivalent region, due to uncertainty in the choice of valence.

The difference in valence choice (2 or 3) for Pr and Nd propagates to a WF shift of about 0.2 eV. Propagation of valence error to the output value in LMTO is unknown.

Compared to Michaelson's lanthanide data, HDFE is closer to experiment than LMTO in five out of nine cases, and in one case the difference is the same. For experimental data taken from Ref. 15, HDFE is better than LMTO in eight out of 12 cases, and in two cases both methods are the same.

TABLE II. Input values for the work function calculations for Fr, Ra, and actinides. Actinide valencies from Refs. 45 and 47, HD and HDFE: this work; mv: calculated from molal volume.

						φ (eV)			
Element	A	ρ (g cm^{-1})	Z	r_s/a_0	E_F (eV)	HD	HDFE	Theory	Expt.
Fr	223	2.60	1	6.12	1.5 (Ref.13)	2.01	2.14	2.13 (Ref.28)	
		1.87	1	6.83			2.02		
Ra	226	5.00	2	4.94	3.0 (Ref. 13)	2.78	3.23	2.03 (Ref. 28)	
Ac	227	10.07	3	2.72	6.10 (Ref. 13)	3.38	3.20	3.44 (Ref. 28)	
Th	232	11.72	3	2.60	7.37 (Ref. 56)	3.28	3.28	3.44 (Ref. 28)	3.3 (Ref. 57) 3.4 (Ref. 15)
Pa	231	15.37	5	2.00			3.73	3.76 (Ref. 28)	
U	238	19.05	6	1.77	15.89 (Ref. 56)	3.97	3.97	3.85 (Ref. 28) 3.82 (Ref. 27)	3.63 (Ref. 15) 3.78 (Ref. 15)
Np	237	20.45	5	1.84			3.90	4.00 (Ref. 28)	
Pu	244	19.82	4	2.02	11.18 (Ref. 56)	3.89	3.72	3.98 (Ref. 28) 3.68 (Ref. 26) (100) 4.14 (Ref. 26) (111)	
Am	243	13.60	3	2.52	6.5 (Ref. 45)	3.7	3.33		
Cm	247	13.51	3	2.54	5.6 (Ref. 45)	3.9	3.32		
Bk	247	14.78	3	2.46	6.4 (Ref. 45)	3.8	3.37		
Cf	251	15.2^{mv}	3	2.45	5.9 (Ref. 45)	4.0	3.38		
Es	252	8.8^{mv}	2	3.37	3.4 (Ref. 45)	3.3	2.88		

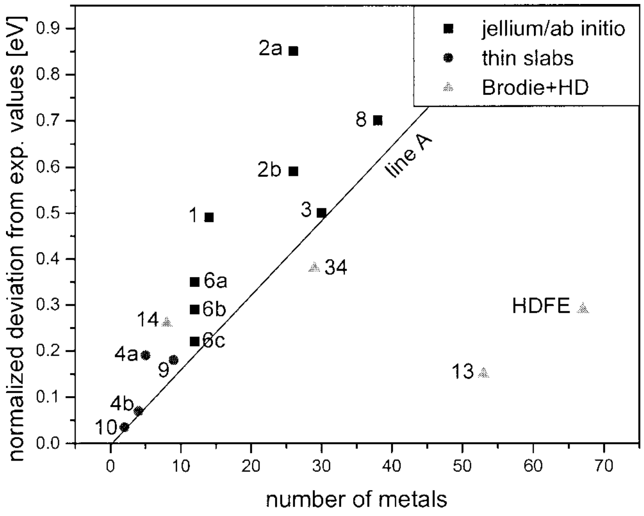

FIG. 1. Comparison of deviation from experimental values for various models of WF. Numbers correspond to references. 2a is for u_c parameter equal $1/\sqrt{3}$, 2b is for $u_c = 1/\sqrt{6}$, 4a is for jellium, and 4b is for pseudojellium, 6a, 6b, and 6d are for jellium, flat surface, and mean value for given faces, respectively.

Altogether, HDFE yields better results than LMTO in 13 out of 21 cases (i.e., in 62%), and equal with LMTO for three lanthanides (14%). If Pr and Nd are assumed trivalent, HDFE surpasses LMTO in 57 and 14% of cases, respectively. It has to be noted that HDFE is done for polycrystalline surfaces, whereas LMTO data are calculated for bcc (110) for Ba and Eu, for hcp (0001) for La, Pr-Sm, Gd-Tm, and Lu, and for fcc (111) for Ce and Yb.

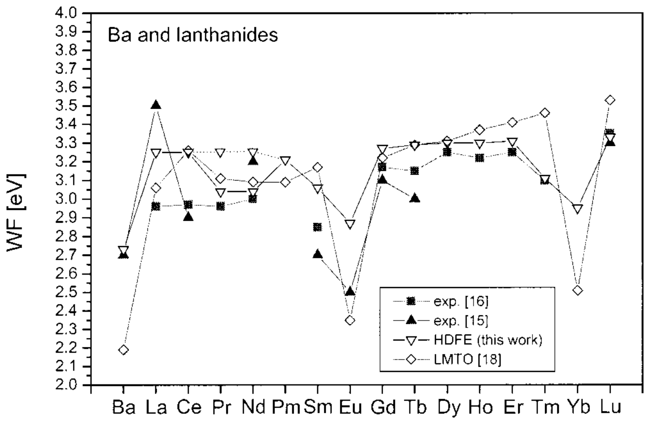

FIG. 2. Comparison of experimental and theoretical WF values for lanthanides. In the case of Pr and Nd, WF was calculated by HDFE for valence 2 (solid line) and 3 (dotted line).

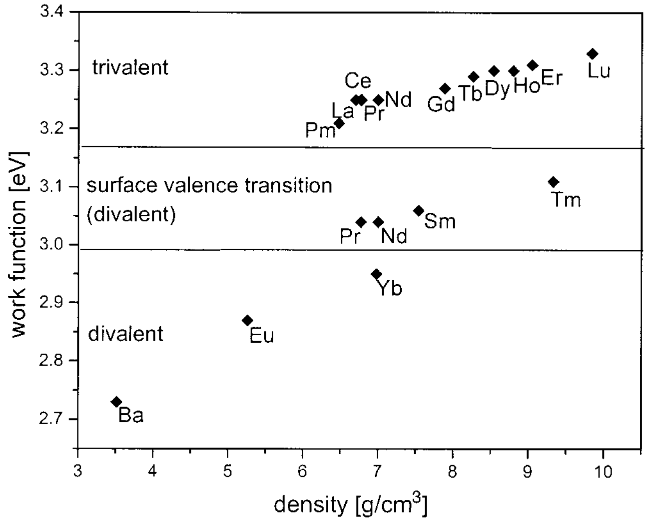

FIG. 3. WF of lanthanides plotted versus density. The surface valence transition is indicated. Pr and Nd are indicated in both valence transition and trivalent ranges.

Values of E_F for Pa and Np were not known to the authors, therefore only HDFE was used for these metals. In Fig. 4 all results for actinides are compared graphically. It may be seen that the agreement with the LMTO method[28] is very good for HD from Fr to Pu, and also for HDFE (except for Ra). Available experimental data for Th show good agreement for all methods: HD, HDFE, and LMTO. LMTO is closer to experimental value for U than HD and HDFE. FLMTO results for U (Ref. 27) are not indicated in Fig. 1, because they cover the range of experimental values. All methods give WF for Pu in the range predicted theoretically by use of FLMTO.[26] Calculation of WF's by Brodie's approach for either lanthanides or actinides produces erroneous values, e.g., 25% smaller than experiment or other theories for U and Pu, unless the effective mass is treated as an adjustable parameter. The authors therefore do not discuss Brodie's model in comparison with other theories and experiments for lanthanides and actinides.

Our results for heavy actinides cannot be compared to other values due to the lack of either calculations or measurements. It may be seen, however, that the agreement between HD and HDFE observed for light actinides is no longer sustained for heavy actinides.

IV. DISCUSSION

The lack of detailed analysis of physical mechanisms is an obvious drawback of any phenomenological approach.

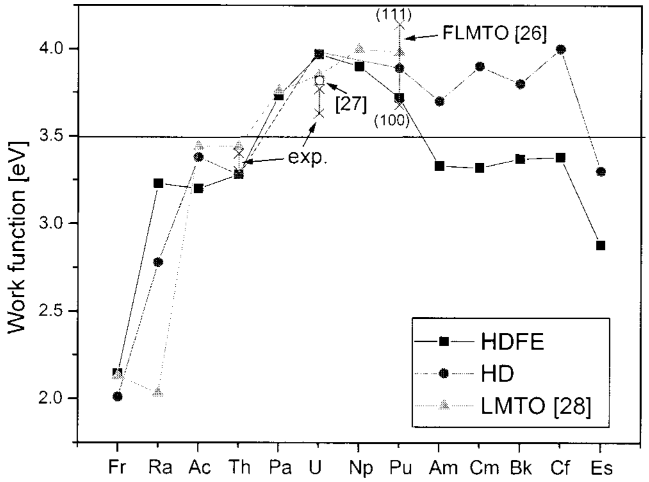

FIG. 4. WF for actinides; comparison of experimental and theoretical results calculated by the use of various methods.

HD and HDFE do not discuss the relativistic or exchange-correlation effects or electron spin. It is assumed that all the electronic properties demonstrate themselves in specific density and/or valence. Only these two parameters combined with either the E_F value (HD) or the atomic mass (HDFE) are used to calculate the WF in HD approaches.[10,38,39]

In order to compare HD with other approaches, it should be recognized that the system to be described ($\sim 10^{23}$ electrons$+10^{23}$ ions) is extremely complicated. Simplifications in *ab initio* approaches, such as the use of pseudopotentials or the single-electron picture, are therefore necessary. The influence of such simplifications on the real system is often unclear[4] and leads to unphysical artifacts like peaking of the WF or surface energy as functions of electron density in Refs. 5 and 7, respectively.

Line A in Fig. 1 shows clearly that *ab initio* models are in fact ''optimized'' for a given group of metals (e.g., alkali metals or transition metals). There are large differences in the electronic structure between, e.g., alkali metals and transition metals, and this is why deviation increases with increasing number of elements. Calculations are therefore usually performed for a few metals of choice only. Work by Skriver and Rosengaard[8] seem to be the only exception from this rule, but their overall agreement with experimental values is very poor. Thin-slab based calculations give the lowest deviations, but results are so far limited to a few metals. It can therefore be suggested that the simple idea of spontaneous polarization used in HD increased the quality of calculation, in the form of agreement with experiment, *more significantly* than any of the advanced attempts to understand the surface influence of the characteristic electronic structure of a metal on the *ab initio* basis.

Another important surface property, namely the surface energy, is systematically about 25% too small if calculated by density-functional calculations.[7] It was already found that simple, non-self-consistent theories of surface energy give much better agreement with experiment than theories based on LDA.[48,49] This is in spite of the fact that some LDA theories do use phenomenological approaches, as it is done in HD, e.g., using correction terms of the order of unity such as multiplicative ''corrugation factor''[6] (similar to the α parameter in HD) or estimation of r_s from the valence.[7]

While *ab initio* models succeeded for alkali metals, which are in any case best described by simple electron gas, none of the *ab initio* models ever reach acceptable agreement with experimental values for transition metals.

Ab initio models have the advantage that they are usually capable to calculate the WF for a given crystallographic face, rather than just for a polycrystalline surface. Attempts to do the same with HD approaches as well as to get rid of the α parameter were undertaken[50] and these preliminary results are encouraging.

In case of lanthanides, it may be seen that the WF is gradually rising from Ba to Lu, except for Ba, Eu, and Yb which have significantly lower WF values than their neighbors. These metals also have significantly lower electron densities than their neighbors. The overall trends of WF, combined with the lowering for Ba, Eu, and Yb are similar in both LMTO and HDFE.

Differences between WF's for specific faces of a metal are usually of the order of 0.2 eV. This would seem to suggest that from the comparison with available experimental data HDFE yields WF's for lanthanides in better agreement with experimental values than LMTO.

Due to the complicated electronic structure of actinides, where the correlated electron behavior is prevalent, it was expected to see a lack of agreement between HD-based and *ab initio* models for these metals. As it may be seen from Fig. 4, however, agreement with experiment is the same for HD, HDFE, LMTO, and FLMTO methods. HD-based and *ab initio* methods are also in agreement with each other.

A discrepancy between HD and HDFE of the order of 0.5 eV occurs for heavy actinides, from Am to Es, where the $5f$ electrons became localized. This surely is caused by extreme simplicity of the HDFE, based on the free-electron picture, which apparently does not describe heavy actinides as well as the light ones. HD for actinides is based on the E_F values calculated by self-consistent *ab initio* methods. However, preliminary comparison of such calculations with photoemission results for Pu show lack of agreement.

Another reason for discrepancy is the $5f$ electron influence on electronic properties of actinides. From Ac to Np the $5f$ electrons are delocalized (itinerant), Pu forms a boundary between Np and Am, and from Am the $5f$ electrons become localized.[51] This difference is accounted for in HD calculations through E_F taken from *ab initio* calculations, but not in HDFE.

In HD and HDFE, the WF calculation problem is reduced to calculation of the distance *d* from which the image force is to be integrated. Up to this distance we face the continuous quantum decoherence[52–54] and beyond *d* only the classical states and classical approaches are required.

The quantum decoherence idea suggests that the environment surrounding a quantum system can monitor the system's observables, the eigenstates of which continuously decohere and finally became classical ones.[54] According to the original idea of Brodie,[14] the quantum decoherence was related to the escaping electron only, decohering from quantum states in the solid to classical states at distance *d*. The failure of the *ab initio* methods documented in this paper indicates that quantum decoherence may refer not only to the electron itself but also to the local band structure of the solid. In the sense of quantum decoherence concept, the act of electron emission from the metallic surface is equivalent to monitoring the system by the environment, and this obviously relates to both the escaping electron and local band structure.

Once the electron leaves the surface, it undergoes decoherence, and also the original band structure at the surface is not preserved. Since an entirely new potential is acting, and no original band structure is preserved, the *ab initio*-based band-structure calculations have to fail, as indicated by line A in Fig. 1.

V. CONCLUSION

Authors do recognize that *ab initio* models are of great value as far as our understanding of solid-state physics is concerned. However, we show here that at present such models are unable to calculate surface properties of metals in accordance with experimental values. Surprisingly, quite a few researchers seem to forget that theory is of value only if agreement with experiment may be documented.

The surface related valence transition concept is verified for Sm and Tm. The existence of such transition for Pr and Nd is suggested. Agreement with experimental data is slightly better for simple HDFE calculation than for *ab initio* modeling, therefore suggesting a need to improve these models in the future. It was shown that the simple phenomenological model predicts the same (within a few percent) values of WF for light actinides as either experiments or LMTO and FLMTO computations. Therefore calculations were extended beyond Pu, which is shown to be an intermediate between localized and itinerant $5f$ systems. In the present authors' view the HD approach gives reliable values of WF for heavy actinides. There is a need for *ab initio* WF data for heavy and experimental data for all actinides. Values of WF for heavy actinides up to Es are calculated and presented.

The beauty of *ab initio* modeling is based on the ability to predict and *give some indication of the kinds of effects to expect*.[55] A first-principles approach describes the physics of the system, but the level of generalization is apparently too high to be used for the calculation of an exact surface property.

The use of a simple phenomenological approach allows us to obtain the best agreement with experiment, which shows the need for better *ab initio* modeling in the future, possibly including the quantum decoherence aspects indicated above.

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*Electronic address: tomasz@lanl.gov

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