High Energy Density Physics xxx (2014) 1–20

Contents lists available at ScienceDirect

High Energy Density Physics

journal homepage: www.elsevier.com/locate/hedp

Continuum lowering – A new perspective

B.J.B. Crowley [a,b,*]

[a] Department of Physics, University of Oxford, Parks Road, Oxford OX1 3PU, UK
[b] AWE PLC, Reading RG7 4PR, UK

ARTICLE INFO

Article history:
Received 9 December 2013
Received in revised form
25 March 2014
Accepted 16 April 2014
Available online xxx

PACS:
52.25.-b
52.25.Jm
52.25.Kn
32.80.-t
32.80.Fb

Other relevant categories:
05.30.-d
05.30.Fk
05.70.-a
05.70.Ce
32.10.Hq
52.27.Aj
52.27.Cm
64.10.+h
71.10.-w
71.10.Ca

Keywords:
Coulomb systems
Ionization potential depression
Continuum lowering
Photoionization
Plasma equation of state

ABSTRACT

What is meant by continuum lowering and ionization potential depression (IPD) in a Coulomb system depends very much upon precisely what question is being asked. It is shown that equilibrium (equation of state) phenomena and non-equilibrium dynamical processes like photoionization are characterized by different values of the IPD. In the former, the ionization potential of an atom embedded in matter is the difference in the free energy of the many-body system between states of thermodynamic equilibrium differing by the ionization state of just one atom. Typically, this energy is less than that required to ionize the same atom *in vacuo*. Probably, the best known example of this is the IPD given by Stewart and Pyatt (SP). However, it is a common misconception that this formula should apply directly to the energy of a photon causing photoionization, since this is a local adiabatic process that occurs in the absence of a response from the surrounding plasma. To achieve the prescribed final equilibrium state, in general, additional energy, in the form of heat and work, is transferred between the atom and its surroundings. This additional relaxation energy is sufficient to explain the discrepancy between recent spectroscopic measurements of IPD in dense plasmas and the predictions of the SP formula. This paper provides a detailed account of an analytical approach, based on SP, to calculate thermodynamic and spectroscopic (adiabatic) IPDs in multicomponent Coulomb systems of arbitrary coupling strength with $T_e \neq T_i$. The ramifications for equilibrium Coulomb systems are examined in order to elucidate the roles of the various forms of the IPD and any possible connection with the plasma microfield. The formulation embodies an analytical equation of state (EoS) that is thermodynamically self-consistent, provided that the bound and free electrons are dynamically separable, meaning that the system is not undergoing pressure ionization. Apart from this restriction, the model is applicable in all coupling regimes. The Saha equation, which is generally considered to apply to weakly-coupled non-pressure-ionizing systems, is found to depend on the Thermodynamic IPD (TIPD), a form of the IPD which takes account of entropy changes. The average Static Continuum Lowering (SCL) of SP relates to changes in potential energy alone and features in EoS formulas that depend on the variation of the mean ionization state with respect to changes in volume or temperature. Of the various proposed formulas, the Spectroscopic (adiabatic) IPD (SIPD) gives the most consistent agreement with spectroscopic measurements.

1. Introduction

1.1. Background

The fact that electrons bound to atoms in plasmas and metals require less energy to liberate them into the continuum than from equivalent states in isolated atoms was, until recently, generally thought to be reasonably well understood to the extent that it could be described in terms of a simple model, despite a lack of sound experimental validation of any such model. Direct spectroscopic observation of ionization potential depression, or continuum lowering as it is sometimes called, is generally frustrated by the Inglis–Teller effect [1] whereby the "true" bound-free edge is obscured through becoming merged with nearby bound–bound transitions. Indirect methods have generally been too imprecise to discriminate between possible alternative models.

Interest in the phenomenon has been revived by some recent spectroscopic measurements [2–4] exploiting new facilities, of dense plasmas, that claim to have circumvented the Inglis–Teller effect to yield good quantitative data. However, rather than confirming the generally accepted thinking, as embodied in the well-known Stewart–Pyatt model [5], for example, they have exposed

* Department of Physics, University of Oxford, Parks Road, Oxford OX1 3PU, UK.
E-mail address: basil.crowley@physics.ox.ac.uk.

http://dx.doi.org/10.1016/j.hedp.2014.04.003

inconsistencies and deficiencies in some well-established current models, and thereby in prior understanding of this phenomenon, while raising deeper questions about the underlying concepts.

In one type of experiment [2,3], a tuneable X-ray laser (FEL) is used to ionize the K-shell in solid-state aluminium. Whether ionization occurs or not is a direct function of the laser energy and is diagnosed by measuring the subsequent Kα emission. The experiment is thus a clean measurement of the spectroscopic ionization potential that does not depend on any underlying model of the subject system. The results of this experiment are illustrated in Fig. 1, in which the observed ionization depression for various ionization states of aluminium is compared with different theoretical predictions. It turns out that the results of this experiment significantly disagree with the predictions of Stewart and Pyatt [5] and are best described by an old model proposed by Ecker and Kröll [6]. This conclusion has raised concerns that the hitherto widely favored model of Stewart and Pyatt is at fault raising concerns over the validity of the large amount of data derived using it.

In another recent experiment [4] spectroscopic measurements are carried out on laser-shocked Aluminium and the presence or absence of the 1–3 lines as a function of temperature and density used as a diagnostic of the continuum lowering. The results of this experiment, and comparisons with various theories, are given in Table 2. While the interpretation of this experiment does depend, to some extent, on modeling of the *in situ* $n = 3$ atomic levels to represent the effect of the various continuum-lowering models, the results appear conclusive and are consistent with a simple ion-sphere model, which is much closer to Stewart and Pyatt than Ecker and Kröll.

Both experiments claim to be able to discriminate between different models of the ionization potential depression with the FEL direct ionization measurement apparently supporting Ecker and Kröll while the laser driven shock measurements are presented as being more consistent with Stewart and Pyatt. Neither model is capable of fitting both experiments.

The Stewart–Pyatt has the virtue of possessing a physics-based derivation, albeit a far from exact one, and incorporates the ion-sphere and Debye–Hückel models in its limits. Simple alternatives, such as Ecker–Kröll, are more *ad hoc* in nature, and/or are of more limited validity, so it is logical that Stewart–Pyatt should carry favor over them. So why experiment should take a contrary view and, in certain circumstances, favor a less well justifiable alternative models seems difficult to understand. Ecker–Kröll depends upon an *ad hoc* assumption, which, even in hindsight, remains unsupported. The application of the ion-sphere model to the

Table 1
Values of the force constant C for various lattices.

Ion sphere	fcc/hcp	bcc	Sc
9/10	0.99025	1.01875	1.09189

laser driven shock experiment does not appear to be justified either, due to the ion coupling being insufficiently strong. Moreover, since all of these models, Ecker–Kröll, Stewart–Pyatt and ion-sphere, claim to model the same thing, any inconsistencies are indicative only of deficiencies in one or more of them. Which model should be used is certainly not a matter of arbitrary choice or preference. While it may be that, of the various models considered, only Stewart–Pyatt appears to be rationally supportable, it is undeniable that *both* sets of experiments clearly demonstrate that the spectroscopically-determined ionization potential depression in dense matter is significantly greater than that predicted by this model.

This is unfortunate. It is not just that a simple formula, like Stewart and Pyatt's, is too useful to discard lightly. While it is true that a detailed atomic physics calculation, using a many-body implementation of density functional theory, for example, that captures the essential physics, might be expected to reproduce observational data, this is not always feasible. This capability is recent and, even now, not all plasma regimes are accessible to such calculations. The formula is incorporated or is implicit in many atomic physics codes still in use or which have been sources of currently available atomic data. So the failure of experiment to support this model is of considerable concern and raises two immediate questions: What is wrong with the model? and Can it be fixed?

This is our starting position. A first step is to review the basis of the Stewart–Pyatt and closely-related formulas to ascertain why they may not yield the results expected of them. Theoretical treatments of continuum lowering typically approach the problem from the point of view of thermodynamic equilibrium. It is true that neither of the experiments is characterized by full thermodynamic equilibrium, but this does not in itself offer a satisfactory or useful explanation for the discrepancies. Continuum lowering features in non-equilibrium situations. In strongly-coupled plasmas, it is largely determined by the potential energy, which is dependent on the spatial configuration of the system independently of whether the system is in thermal equilibrium. Nevertheless, it is the presumed connection with equilibrium that turns out to be very much at the heart of the matter.

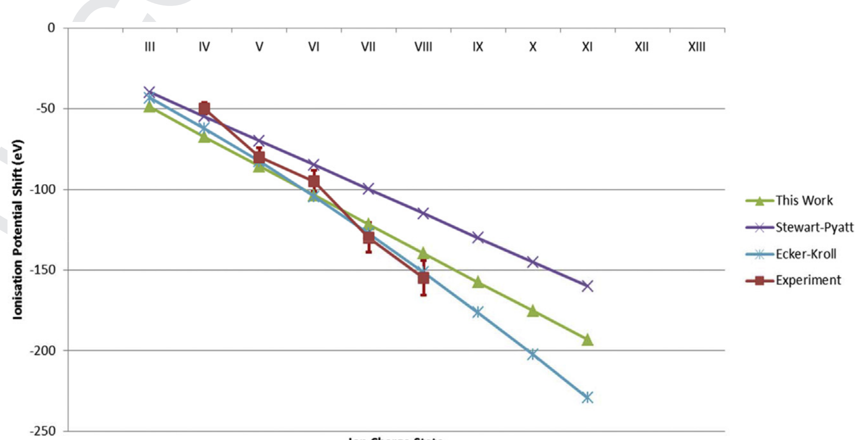

Fig. 1. Calculations of the ionization potential depression for various ion charge states in solid density aluminium compared with the measurements of Ciricosta et al. [2]. Stewart–Pyatt is equation (12), Ecker–Kröll is (169) and "This Work" is equation (81).

Please cite this article in press as: B.J.B. Crowley, Continuum lowering — A new perspective, High Energy Density Physics (2014), http://dx.doi.org/10.1016/j.hedp.2014.04.003