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The pseudopotential for quadrupole fields up to q = 0.9080

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ABSTRACT

Pseudopotential models for radio frequency (rf) electric fields are widely used. However, these approximate and sometimes intuitively introduced methods, can sometimes lead to ambiguities and false conclusions. While a classical model works well for quadrupole fields with small q where the Mathieu parameter $\beta \le 0.4$ there has been some discussion in the literature of the behavior of a pseudopotential, and, in particular, the secular frequency of ions for larger q near the far end of the stability zone (for example, near $q_{max} \approx 0.908045$ for $a = 0$). This paper analyzes carefully the behavior of secular frequencies calculated both numerically and analytically and demonstrates that the classical formula for the secular frequency in the pseudopotential, $\omega = \beta\Omega/2$ remains valid up to $\beta = 1$. This means that both the secular frequency and the pseudopotential function well depth increase monotonically with q inside the stability zone. However, some models state that the well depth, identified as the pseudopotential function calculated at the edge of a quadrupole aperture, should be zero at both the low q and high q boundaries of the stability zone, with a maximum somewhere between. It is shown that the paradox that the acceptance is zero at both ends of the stability zone and hence the pseudopotential well depth and the pseudopotential quadratic coefficient should be zero at both boundaries of the stability zone is resolved by introducing for large q a pseudopotential well depth and a pseudopotential well width as separate pseudopotential objects to characterize the acceptance, while a quadratic pseudopotential function is used to describe the secular motion of ions but not the acceptance for large q.

1. Introduction

The concept of a pseudopotential function [1–3] has often proved useful for charged particle optics. It also proves its effectiveness in the description of an ensemble of ions which move in radio frequency (rf) quadrupole fields [4–11]. Although it is an approximate way to describe ion motion in radio frequency electric fields, it gives useful hints how a particular radio frequency system operates and how some radio frequency systems should be created and optimized to operate in a desired way. However, it should be kept in mind that this is a qualitative, not a quantitative way to describe ion motion in radio frequency electric fields and that the actual behavior of ions should always be verified by strict methods (for example, numerically).

Starting with Paul's invention of the radio frequency quadrupole ion trap and the radio frequency quadrupole mass filter [12–14] quadrupole electric fields have been of continual interest. The pseudopotential approach was used successfully to explain and to analyze the basic behavior of general rf devices [4–11] and, in particular, of quadrupole devices [15–18]. Quite often the pseudopotential is used to explain qualitatively the behavior of ions in quadrupole rf fields by representing the true motion as an approximate (averaged, or slow) motion inside a sum of a quadratic dc potential and an effective quadratic rf pseudopotential. The resulting quadratic and mass dependent pseudopotential distribution produces the spatially localized harmonic oscillations of ions of specific masses and explains transparently in some cases the stable mode of ion motion for the rf quadrupole field [2–5,8,19].

However, exact rf quadrupole theories (i.e. the Mathieu and Hill equations [20–23]) demonstrate not only the power of the pseudopotential method but also its weakness and limitations. In particular, the Landau pseudopotential function [1–3] as applied to quadrupoles [4,5] cannot explain the existence of numerous stability zones or even the appearance of the far end boundary of the first stability zone

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(i.e. $q_{max} \approx 0.908045$ for $a = 0$, for example). However, ion motion near the entry boundary (at low q) of the first stability zone is described by the pseudopotential method with reasonable accuracy [4,5,24,25].

The utility and simplicity of the pseudopotential approach led several authors to modify the Landau pseudopotential theory [1–3] in such a way that its weak points are eliminated. Dehmelt [4,5] showed that for a 3D ion trap an effective potential [1–3] can, with some operating conditions, be used to describe the motion of ions confined in a quadrupole field for moderately small q. Sudakov [17] proposed that the beat-like ion motion at high q could be described as motion in an effective potential with a modified well depth. Later, Sudakov and Apatskaya proposed another model [18] for high q suitable near the tip of the stability zone which is based on the beats of the stroboscopic samples instead of the secular oscillations. Konenkov et al. [24] described the matrix method which exactly describes the secular oscillations of the stroboscopic samples without use of a pseudopotential model. Although the use of the pseudopotential is often restricted to q values less than 0.4, Makarov showed it could be used to give quite good agreement with experimental measurements of mass resolutions of ions resonantly ejected at q = 0.84 from a quadrupole trap [9]. Baranov et al. [26] numerically calculated kinetic energies of ions confined in a linear quadrupole with q values from 0.20 to 0.85 and showed that they generally increase with q since the trapping forces increase because of higher rf voltages applied to the quadrupole (this result calls into question the statements in [17,18] that the pseudopotential function and the pseudopotential well depth decrease at high q). By introducing different pseudopotential concepts for the quadrupole secular frequencies and for the quadrupole acceptances the publication [27] resolves the contradiction between the monotonic increase of secular frequencies with increasing q and the decrease of quadrupole acceptance when q is large and is near q_{max}. Reilly and Brabeck [28,29] proposed to get the quadratic coefficient of a pseudopotential function directly from secular frequencies of Mathieu-Hill equations using the numerically or analytically calculated trace of a monodromy matrix, as used in [27]. However, their formula is artificially modified in such a way that both the secular frequency and the pseudopotential well depth decrease to zero near the far end of the stability zone. Douglas and Gao [25] tried to determine directly a true pseudopotential value by looking for the displacement in numerical simulations of the equilibrium point of ions influenced both by an electric rf quadrupole field and a dc dipole electric field. Their results confirm that Dehmelt's classical formula [4,5] for the well depth is true nearly till the end of the stability zone (at least for the case with no dc quadrupole potentials). However, it seems that these results should be revisited since the combined action of a dipole excitation (dc, ac or rf) and a quadrupole rf field on ion motion is not reduced to a simple superposition of a dc dipole barrier and a pseudopotential quadrupole barrier.

Briefly, Sudakov [17,18], Douglas et al. [27], and Reilly and Brabeck [28,29] have independently suggested modifications of the pseudopotential model which should retain its validity for quadrupole rf fields over a wide range of q. These theories differ mathematically which is not a suspicious matter by itself. (For example from Werner Heisenberg's and Erwin Schrödinger's versions of quantum mechanics we know that quite different mathematical descriptions can describe the same physics.) However, these theories of the pseudopotential differ physically; they cannot all be correct.

Namely, both [17,18] and [28,29] state that the quadratic pseudopotential well depth increases from zero at the entry boundary of the stability zone (at $q = 0$ for $a = 0$), then has a maximum (actually a downturn, a break in its smoothness with keeping its continuity) inside the stability zone, after which it decreases to zero at the exit boundary of the stability zone, naturally becoming negative outside the stability zone. However, [27] states that the quadratic pseudopotential grows monotonically and smoothly from zero at the entry boundary of the stability zone till the exit boundary of the stability zone where it has a positive maximum and an instant jump to negative values corresponding to instability of ions. The theory of Reilly and coworkers [28,29] predicts that the secular frequency is zero at both boundaries of the stability zone with a maximum between, while [27] predicts that the secular frequency ω grows monotonically from zero at the entry boundary to $\Omega/2$ at the exit boundary (where Ω is the rf angular frequency). Both [17,18] and [28,29] state that the loss of stability is due to the fact that the quadratic pseudopotential changes its sign, the pseudopotential barrier smoothly changes its concave profile into a flat (zero) and a convex one at the far stability boundary ($q \approx 0.908045$ for $a = 0$) which implies the soft appearance of instability of ions. Contrary to these publications [27] states that this qualitative description is true at the entry boundary of the stability zone while at the exit boundary of the stability zone a loss of stability is due to a parametric resonance between secular (self) ion oscillations with a frequency $\Omega/2$ and forced ion oscillations with a frequency Ω caused by the radio frequency electric field (see [1,p. 80–84] for more details about parametric resonances). The latter means a sudden appearance of instability at the exit boundary of the stability zone. The other questionable point of the theories under consideration is the use of the pseudopotential well depth alone to describe the acceptance of an rf quadrupole which results in incorrect asymptotic behavior of the acceptance for large q; this is discussed in Section 5.

The said qualitative description by the theories [17,18,27–29] which modify the Landau classical approach [1–3] specifically for quadrupoles applies to all zones of stability, not just the first zone, and to arbitrary periodic radio signals, not necessarily only to sinusoidal waveforms. However, the differences between these theories are too serious to ignore. The purpose of this paper is to clarify which statements are correct.

2. Definitions

The main point of this publication is the following. What is typically called by the generic term 'pseudopotential' for small q is split into several independent objects for large q. As a result it is necessary to introduce different definitions for these objects because they correspond to different mathematical constructions. To help the reader, all new definitions are concentrated in this section. The reasons for introducing these definitions and the mathematical expressions hidden behind them are explained only later in the paper.

2.1. *Pseudopotential model (pseudopotential approach)*

The method to describe the motion of charged particles in periodic or quasi-periodic rf electric fields where the motion is separated into 'slow' motion defined by some stationary differential equations and 'fast' motion containing the rf oscillations of the trajectory induced by the time-dependent rf electric field [1–3].