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Ab initio Mg-(He^0,He^+,He^{2+}) potentials and ion scattering by atomic strings and planes

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Results of *ab initio* calculations for the interaction energy of the Mg-He^0, Mg-He^+, and Mg-He^{2+} systems are presented, for a wide range of internuclear distances. The importance of using *ab initio* methods for the evaluation of accurate pair-wise potentials is discussed. A strong dependence of the interaction energy on the charge state of the projectile is demonstrated. This effect, which exhibits marked deviations from the predictions of any parametric theory, is shown to be also crucial in the behavior of corresponding string and planar potentials commonly used in both experimental channeling and surface scattering studies. The role of long-range binary terms on the construction of string and planar potentials is also discussed.

I. INTRODUCTION

In studies of the interaction of energetic ions with solids the atomic interaction potential is always of central importance.[1,2] Recent years have seen the advent of a number of different experimental measurements, all highly sensitive to the details of the interatomic potential operating between the colliding partners[3–7] and all demonstrating the need for accurate estimates of the interaction energy, especially over the smaller interatomic distances, where there is repulsion. In addition, there has been a rapidly growing interest in theoretical methods directed at deriving, from first principles, the interaction potentials to be used in collision theory.[8–11] In the present studies, instead of employing empirical potentials, a binary potential is adduced using *ab initio* molecular-orbital procedures. The increasing attention being paid to *ab initio*, as opposed to empirical or parametric potentials, is due both to clear discrepancies observed between the former and the latter and to marked inadequacies revealed in parametric potentials when attempts are made to use them in explaining quite sophisticated experimental range determinations[7] and ion-surface scattering studies.[11]

The work we describe here is devoted to the *ab initio* potentials for the Mg-He^0 system and for the corresponding ionic states Mg-He^+ and Mg-He^{2+}. A strong dependence of the interaction energy on ionic charge is observed, showing marked deviations from the predictions of any universal parametric theory presently available. A proper parametrization is suggested for the complete range of internuclear distances considered. Application to the construction of continuum string and planar potentials[12,13] is also discussed, as is the effect of long-range binary forces on the calculation of these potentials.

II. METHOD

A molecular-orbital method was used to obtain the Mg-He^0, Mg-He^+, and Mg-He^{2+} interaction potentials. The basic computer program was PSHONDO, a modified version of the earlier HONDO program,[14] which includes the *ab initio* potentials of Barthelat *et al.*[15] These pseudopotentials are now widely used and have been found to agree well with all-electron calculations. In particular, they have been successfully applied to systems which include monovalent and divalent cations.[16]

Since we were particularly interested in constructing the interaction potential for relatively small internuclear distances (well into the repulsive wall), care had to be taken in considering the validity of the pseudopotential model for this region. A correction term (core correction) due to the neglected repulsion between the frozen core of the magnesium atom and the helium nucleus had to be included. This term was evaluated in the following way. First, the ground-state energy of the Mg^{2+}-He^{2+} system was computed with all the electrons treated explicitly. Then, in order to ensure a frozen core, this energy value was taken to be that of the first self-consistent-field (SCF) iteration, with the antisymmetrized product of the atomic wave function as the trial function. From the above energy we subtracted the nuclear repulsion plus the total energies of the isolated Mg^{2+} and He^{2+} systems, thus yielding the desired core correction. In order to verify the adequacy of such a corrective procedure three different pseudopotentials, PS-I, PS-II, and PS-III (allowing, respectively, 2, 8, and 10 electrons of Mg to be considered explicitly), were used to calculate the interaction energy for the various internuclear separations of the Mg-He^0 system at the SCF level. Table I shows the results of such calculations.

TABLE I. Comparison of the interaction energies (in a.u.) for the Mg-He system in the strongly repulsive region of the three different pseudopotentials (see text).

R (a.u.)	PS-I ($z=6$)	PS-II ($z=8$)	PS-III ($z=10$)	PS-I + core correction
1.00	2.7351	3.1103	3.2178	3.2224
1.50	0.9590	1.0243	1.0193	0.9961
1.75	0.5796	0.5945	0.5835	0.5900

It is readily apparent that the Mg pseudopotential which treats explicitly only the valence electrons (PS-I) can be used for internuclear distances as short as 2.0 a.u. Furthermore, for separations down to 1.0 a.u., the core correction is very appropriate. Accordingly, all calculations made for distances shorter than 2.0 a.u. were corrected in the manner described above. Specific parameters for the three pseudopotentials used in the calculations are reported elsewhere.[16] We note at this stage that, in performing this correction, we have invoked the frozen-core approximation characteristic of pseudopotentials. The core of Mg is assumed to be the same in the presence of He, He^+, or He^{2+}. Nonetheless, we will be referring to our results as *ab initio*, so as also to distinguish them from those obtained by empirical or semiempirical methods.

The basis set used for testing the adequacy of the procedure to compute the core correction was of a double-zeta-plus-polarization quality, i.e., four Gaussians contracted {3,1} and one p-polarization function on each atom. The basis set used for computation of the energy profiles was of a triple-zeta-plus-polarization type, i.e., five Gaussian functions contracted {3,1,1} and three p-polarization functions. The Gaussian exponents were optimized in atomic pseudopotential calculations using the ATOM program.[17] Table II displays the numerical values for the basis set.

All calculations were performed with an SCF plus configuration-interaction (CI) procedure in order to include the correlation energy. All valence CI calculations were made according to an improved version[18] of the CIPSI algorithm,[19] which combines variational and perturbation techniques. A variational zeroth-order wave function is built from an iterative selection of the most important determinants, the others being taken into account through a second-order Moller-Plesset perturbation. All determinants having a coefficient larger than 0.03 in the first-order wave function obtained by perturbation have been included in the zeroth-order wave function at the final step. The number of determinants in the zeroth-order wave function was 23 for Mg-He^0, 70 for Mg-He^+, and 44 for Mg-He^{2+}, and all ground states were of Σ symmetry.

Before proceeding, we emphasize that it is necessary to be aware that the dissociation limit for the ground state of the $(\text{Mg-He})^+$ system is $\text{Mg}^+(^2S)$-$\text{He}(^1S)$. Due to the Rydbergization of the excited states of magnesium, there exists a multitude of other states between $\text{Mg}(^1S)$-$\text{He}^+(^2S)$ and the former, with the same symmetry and high transition probabilities between them. Their relative energy positions can be constructed from the experimental ionization potentials.[20] It is clear then that a realistic potential curve under these conditions would require a detailed (and costly) study of the whole spectral region, involving a great number of excited states. In this work we have restricted ourselves to the potential curve of a single electronic state of the $(\text{Mg-He})^+$ system, namely, the $\text{Mg}(^1S)$-$\text{He}^+(^2S)$ state. The results will therefore apply mainly to keV ion-surface scattering (and channeling) processes, where the collision time will be rather short (in contrast to reactive collisions in quantum chemistry), and where we may accordingly expect that the probability of transition between different electronic states will be small. As a consequence, for practical purposes the assignment to one particular state can in this case be justified. In an analogous manner a similar approximation was made for the Mg-He^{2+} state. In this case we found an avoided crossing in the region between 6.0 and 9.0 a.u. with a potential curve corresponding to an excited state of the Mg^+-He^+ system, as shown in Fig. 1. Since transitions

TABLE II. Atomic Gaussian basis sets used in this work.

	Mg		He	
Orbital symmetry	Exponent	Contraction coefficient	Exponent	Contraction coefficient
s	1.661 910	0.063 918	56.713 556	0.014 839
	0.785 243	−0.276 456	8.899 423	0.091 507
	0.134 225	0.340 769	2.296 068	0.260 238
	0.071 435	1.0	0.890 058	1.0
	0.033 260	1.0	0.280 503	1.0
p	2.80	1.0	4.50	1.0
	0.20	1.0	0.37	1.0
	0.07	1.0	0.05	1.0

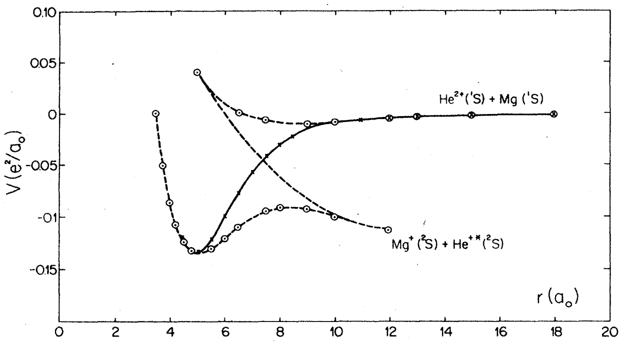

FIG. 1. *Ab initio* results for the Mg-He^{2+} system showing an avoided crossing with an excited state of Mg^+-He^+ (see text).

between different states are being neglected, an interpolation for the potential in the crossing region was carried out in such a way as to consider only the potential curve for the $Mg(^1S)$-$He^{2+}(^1S)$ throughout the whole range. Consequently, whenever we refer to the He^+ or He^{2+} systems interacting with one or more Mg atoms, we shall tacitly assume the validity of this single-state curve.

III. RESULTS AND DISCUSSION

A. *Ab initio* binary potentials

The values of the *ab initio* interaction energies for the Mg-(He^0,He^+,He^{2+}) systems are presented in Table III. In the case of the Mg-He system we have found that the correlation energy has a nearly constant value (−0.058 a.u.) over the range of interatomic distances treated, in agreement with the results of Demetropoulos *et al.*[10] As a consequence of this, correlation has a negligible effect on the interaction energy, as may be verified from Table III, and so the results at the SCF level are quite adequate for study of the system in this region. On the other hand, for the Mg-He^+ and Mg-He^{2+} systems it becomes necessary to include the effects of correlation since it gives rise

TABLE III. *Ab initio* interaction energies (in a.u.) for the systems considered in this work.

R (a.u.)	$E(He^{2+}$-$Mg)$[a]	$E(He^+$-$Mg)$[a]	$E(He^0Mg)$[b]	$E(He^0$-$Mg)$[c]
1.0	2.9423	2.8286	3.0139	
1.5	1.3290	1.1557	0.9656	
2.0	0.7467	0.5750	0.3291 (0.3275)	0.3306
2.5	0.4133	0.3335	0.1332	0.1319
3.0	0.1619	0.1935	0.0678	0.0679
3.5	−0.00003	0.1023	0.0404	0.0406
3.75	−0.0508			
4.0	−0.0862	0.0461	0.0249 (0.0250)	0.0327
4.25	−0.1097			
4.5	−0.1240	0.0147	0.0150	
4.75	−0.1315			
5.0	−0.1340	−0.0012	0.0087 (0.0085)	0.0090
5.25	−0.1330	−0.0056		
5.5		−0.0086		
5.75	−0.1253	−0.0104		
6.0	−0.1200	−0.0115	0.0026 (0.0025)	
6.25		−0.0119		
6.50	−0.1091			
6.75		−0.0115		
7.0		−0.0110	0.0006	
7.5	−0.0934	−0.0097		
8.0	−0.0905	−0.0083	0.00010 (0.00011)	
8.5		−0.0069		
10	−0.0080			
11	−0.0060			
12	−0.0044			
13	−0.0032			
15	−0.0019			
18	−0.0009			

[a] SCF energies.

[b] SCF + CI values are given in parentheses. Energy referenced to total energy at $R = 40$ a.u.

[c] SCF + CI energies from Ref. 10.

to substantial modifications of the SCF values. The final corrected values for the three systems are presented in Table III. As will be seen, both ionic states show a clearly defined minimum: at a distance of 6.25 a.u. with a depth of 0.0119 a.u. for Mg-He^+ and at a distance of 5.00 a.u. with a depth of 0.1330 a.u. for Mg-He^{2+}.

B. Parametrization of the potentials

In order to make best use of the *ab initio* results in practical applications, an analytical representation of the corresponding curves is desirable. Careful analysis of the results presented in Table III immediately suggests parametrization of the *ab initio* potentials for each ionic state of the Mg-He system in a manner analogous to that used recently by Cruz *et al.*[9] This comprises a Bohr-type term representing the core-core repulsion, and dominant at very small interatomic distances, plus a Born-Mayer–type term for the softer valence part, written as follows:

$$V_0(R)=\frac{Z_1Z_2}{R}(ARe^{-\alpha R}+e^{-\beta R}) , \tag{1}$$

in atomic units (e^2/a_0, where a_0 is the Bohr radius). R is here the interatomic distance (in units of a_0), Z_1 and Z_2 are the atomic numbers of each atom, and A, α, and β are quantities which are obtained from adjustment to the *ab initio* results.

The strong change in curvature observed in the case of the ionic systems for intermediate nuclear separations may be explained in terms of an induction energy, due fundamentally to the interaction between the ionic charge and the polarized electronic cloud of the neutral system. It is well known[21,22] that the multipolar character of the induction interaction as well as parity considerations of the ion-atom states produce relevant long-range terms which behave as R^{-4} (charge–induced-dipole) and R^{-6} (induced-dipole–induced-dipole). In this connection we could, in principle, perform a parametrization which should come as close as physically possible to a more realistic expression with the functional form

$$V(R)=V_0(R)+C_1R^{-4}+C_2R^{-6} , \tag{2}$$

with V_0 given by Eq. (1), and where the constants C_1 and C_2 could be obtained in terms of adjustable parameters which yielded a good fit to the *ab initio* points. In this work, however, we have chosen an alternative expression for the long-range terms which is simple and permits an accurate description over the full range of internuclear distances considered. We accordingly propose the following expression for the Mg-He^0 and Mg-He^+ systems:

$$V(R)=V_0(R)-CR^{-6}\exp(-\gamma R^{-4}) , \tag{3a}$$

where V_0 is again given by Eq. (1), and C and γ are quantities obtainable from the *ab initio* results. For the Mg-He^{2+} system, we propose the alternative expression (see below)

$$V(R)=V_0(R)-CR^{-6}\exp(-\gamma R^{-1}) +C'R^{-5}\exp(-\gamma' R^{-3}) , \tag{3b}$$

where C' and γ' are also obtained from adjustment to the *ab initio* results. The numerical values of the parameters A, C, C', α, β, γ, and γ' are displayed in Table IV.

It is certainly worth mentioning at this stage that the exponential factors appearing in the long-range terms in Eqs. (3) serve the purpose of providing a rapid cutoff as R decreases. It is also stressed that, although chosen on the basis of physical intuition, no direct physical meaning may be assigned to these terms unless this functional form is used consistently with Eq. (2). In their present form Eqs. (3) constitute simply an accurate description of the *ab initio* potentials over the range of distances studied. The extra term appearing in Eq. (3b) is a direct consequence of the fact that, for this system, an avoided crossing occurs at medium distances. This behavior cannot be reproduced by a single R^{-6} term. As may be clearly seen from Fig. 1, the *ab initio* points deviate from the parametrized curve in precisely the manner to be expected due to the presence of the competing state.

Equations (3) have been used to parametrize the *ab initio* results for the entire range of interatomic distances reported. The results are shown in Fig. 2. For distances less than 0.5 a.u., the Thomas-Fermi-Molière potential was considered as an asymptotic limit since the *ab initio* potentials coalesce into a single curve (see Fig. 2) suggesting, as expected, correct and proper use of universal potentials for very short interatomic distances. It is to be noted that inclusion of the long-range terms permits an extremely satisfactory description over a wide range of interatomic distances. In particular, the very good agreement of the parametrized potential with the *ab initio* results for the Mg-He^{2+} system at large distances ($R \gtrsim 10$ a.u.) should be noted.

Although for the neutral (Mg-He^0) system the region of the potential minimum is not contained in our calculations, the corresponding parametrized potential predicts the existence of such an extremum at $R=9.8$ a.u. with an energy of -6.76×10^{-5} a.u. Recent full-CI calculations of Chiles and Dykstra[23] with a saturated basis set show the existence of a minimum at $R=10.6$ a.u. with an energy of -1.0×10^{-5} a.u. for this latter system. This agree-

TABLE IV. Numerical values of the parameters used in the analytical expressions to fit the *ab initio* potentials (all values in atomic units).

System	A	α	β	C	γ	C'	γ'
He^0Mg	0.0542	0.9921	2.2500	158.13	1888.8		
He^+-Mg	0.2083	1.0530	3.0030	6300.0	67.578		
He^{2+}-Mg	0.2580	1.0415	3.6652	536 366.0	26.437	5650.0	700.0

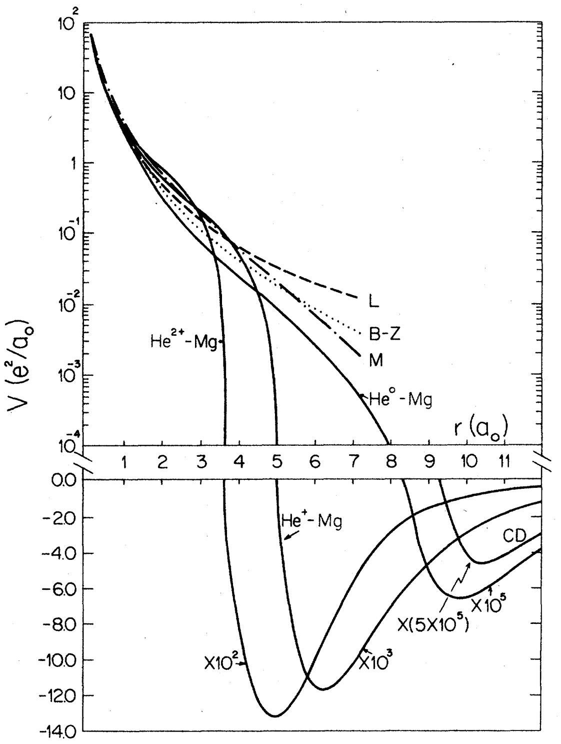

FIG. 2. Potential-energy curves for the parametrized *ab initio* potentials. The curve labeled *CD* corresponds to an alternative parametrization including the van der Waals minimum reported in Ref. 23 for the neutral case (see text). Also included are the following selected universal potentials: (*L*) Lindhard (Ref. 12), (*B-Z*) Biersack-Ziegler (Ref. 24), and (*M*) Thomas-Fermi-Molière (Ref. 2). Note the changes of scale.

ment may be construed as an expression of confidence in the choice of the analytical potential function employed, if we take into account the small numerical values involved. However, there remains a large percentual discrepancy regarding the depth of the potential well, which is of a van der Waals type. Of course, attempts to reproduce such a small value with the basis set here considered were not successful. We did not perform the calculation in the region of the van der Waals well due to the large computational cost involved in "saturated" calculations. However, we have used the results of Chiles and Dykstra for the position and depth of this potential well in order to properly account for it. The curve labeled *CD* in Fig. 2 corresponds to an alternative parametrization which, in addition to our *ab initio* points, includes values reported by these authors. In this case the parametrized potential takes the form

$$V_{CD}(R)=V_0(R)-CR^{-10}\exp(-\gamma R^{-4}) \ , \qquad (3c)$$

with $C=1.13\times10^6 e^2 a_0^9$ and $\gamma=4394.45a_0^4$.

Together with the parametrized potentials, Fig. 2 shows the predictions of several universal potentials widely referred to in the literature.[1,2,12,24] It is readily apparent that for internuclear separations of about 1.0 a.u. the *ab initio* and universal potentials tend to coalesce into a single curve. However, for intermediate distances and beyond, quite marked deviations are evident. A very strong dependence of the potential-energy curve on the projectile charge state is observed in the *ab initio* results. For instance, even though the region between 1.0 and 2.0 a.u. is characterized by the same qualitative behavior, there are relatively large differences in the numerical values. The Biersack-Ziegler potential[24] provides a reasonable average over the three curves for the repulsive component. At still larger distances the marked minimum shown by the ionic systems is, of course, not at all found in the predictions of the universal potentials.

The pairwise interaction potentials described here may be directly used in studies of the penetration of ions into solids. In this case the neutral system may well be the most appropriate, because of the high probability of neutralization of a moving ion as its velocity decreases. So far, penetration studies dealing with range calculations have employed the repulsive part of the interaction only, with quite satisfactory results provided that accurate pairwise potentials are used (see, for example, Refs. 6, 7, and 11). On the other hand, surface scattering and planar and axial channeling experiments with low-energy ion beams (energies above 1 keV) apparently show good agreement with calculations using continuum string and planar potentials[13] based on the superposition of the gas-phase pairwise repulsive interaction of projectile and solid atom. As a consequence, more accurate and reliable descriptions of the basic interaction are also now being increasingly used for the construction of continuum potentials.

C. String and planar potentials

According to Lindhard,[12,13] there is a direct and fundamental relationship between the basic pairwise potential and the continuum string and planar potentials derived from it:

$$V_s(z)=d^{-1}\int_{-\infty}^{\infty} V(\sqrt{x^2+z^2})dx \ , \qquad (4)$$

$$V_p(z)=2\pi N d_p \int_0^{\infty} V(\sqrt{\rho^2+z^2})\rho\, d\rho \qquad (5)$$

(for continuum string and continuum planar potentials, respectively), where z is the distance from the projectile to the string or plane and where, as usual, d is the interatomic distance between neighboring atoms in the string. The product Nd_p in Eq. (5) represents the average number of atoms in a plane, with N the atomic density and d_p the distance between atomic planes in the crystal. Finally, V is the binary potential between the projectile and an atom in the plane (string).

As we shall see further below, Eqs. (4) and (5) are particular cases of a more general expression involving the periodicity of the surface lattice. Following Cabrera *et al.*[25,26] the total potential between the projectile and the solid surface may be expressed as the Fourier sum:

$$v(r)=\sum_G v_G(z)\exp(i\mathbf{G}\cdot\mathbf{R}) \ , \qquad (6)$$

with $\mathbf{r}=(x,y,z)$ the position vector of the projectile with respect to an origin fixed at the surface, $\mathbf{G}$ a twodimensional reciprocal surface lattice vector (see Ref. 25), and $\mathbf{R}$ a vector on the surface such that $\mathbf{r}=(\mathbf{R},z)$. The expansion coefficients v_G are readily obtained:

$$v_G(z)=s^{-1}\int_s v(\mathbf{R},z)\exp(-i\mathbf{G}\cdot\mathbf{R})d^2\mathbf{R}\ , \tag{7}$$

where the subscript s indicates integration over a unit surface cell of area s. If the interaction potential between a given projectile and the solid is written as the direct superposition of projectile and solid-atom pairwise potentials then

$$v(\mathbf{R},z)=\sum_N V(|\mathbf{r}-\mathbf{r}_N|)\ , \tag{8}$$

where $\mathbf{r}_N$ denotes the vector position of an atom in the solid and the sum is taken over all N atoms. Using Eqs. (7) and (8), and taking into consideration the different planes p that form the solid, Cabrera obtains finally for the expansion coefficients

$$v_G(z)=2\pi s^{-1}\sum_{p=0}^{\infty}\exp(ip\mathbf{G}\cdot\mathbf{R}_3)\times\int_0^{\infty}V\{[\rho^2+(z+p v_z)^2]^{1/2}\}\times J_0(\rho G)\rho\,d\rho\ , \tag{9}$$

where $\mathbf{R}_3$ is the tangential component of a primitive vector entering the surface with a normal component $v_z\hat{k}$ (v_z not necessarily an integer), ρ is the magnitude of the tangential component of the vector $\mathbf{r}-\mathbf{r}_N$, and J_0 is the zeroth-order Bessel function.

The physical meaning of the expansion coefficients, $v_G(z)$, has been discussed by several authors.[25,27] The case $G=0$ represents the average of the projectile-surface interaction, while the $G\neq 0$ components correspond to diffracting potentials in atom-beam diffraction experiments. Moreover, for a single plane of atoms the average potential ($G=0$) given by Eq. (9) reads as follows:

$$V_0(z)=2\pi s^{-1}\int_0^{\infty}V(\sqrt{\rho^2+z^2})\rho\,d\rho\ , \tag{10}$$

which corresponds to the continuum planar potential [Eq. (5)] proposed by Lindhard. An equivalent expression for the continuum string potential [Eq. (4)] may be readily obtained from Eq. (9) if we recognize that the string is a particular case of the plane.

An important feature of the average string and planar potentials given by Eqs. (4) and (10) is that they do not depend functionally on the detailed crystal structure of the solid, except for the area of the unit cell, s, in Eq. (10) (e.g., for a simple cubic lattice $s=d^2$ and for face-centered cubic $s=\frac{1}{2}d^2$).

The quantity of importance is the pairwise potential V. We now use Eqs. (3), (4), and (10) to construct the average planar (string) potentials for the He^0, He^+, and He^{2+} systems and a plane (string) formed by Mg atoms, paying particular attention to the effect of the long-range attractive terms of the binary interaction on the string and planar potentials, respectively.

Substituting the binary potentials for the Mg-(He^0,He^+,He^{2+}) systems into Eq. (4), the corresponding string potentials are obtained as follows:

$$V_s^0(z)=I_s(z)-Cd^{-1}z^{-5}\int_0^1 dx\sqrt{x/(1-x)}g(x)\times\exp(-\gamma x^2/z^4)\ , \tag{11a}$$

with

$$g(x)=\begin{cases}x\\ z^{-4}x^3\end{cases} \tag{11b}$$

[using Eqs. (3a) and (3c), respectively],

$$V_s^+(z)=I_s(z)-Cd^{-1}z^{-5}\int_0^1 dx\sqrt{x/(1-x)}\times x\exp(-\gamma x/z^2)\ , \tag{11c}$$

$$V_s^{2+}(z)=I_s(z)-2Cd^{-1}z^{-5}\times\int_0^1 dx\,x^4/\sqrt{1-x^2}\exp(-\gamma x/z)+C'd^{-1}z^{-4}\int_0^1 dx\,x/\sqrt{1-x}\times\exp(-\gamma' x^{3/2}/z^3)\ , \tag{11d}$$

where $I_s(z)$ is the contribution from the repulsive term,

$$I_s(z)=\frac{2Z_1Z_2}{d}[AzK_1(\alpha z)+K_0(\beta z)]\ . \tag{11e}$$

A, C, C', α, β, γ, and γ' are the parameters with corresponding values given in Table IV, and K_0 and K_1 are modified Bessel functions of the zeroth and first order, respectively.[28] Similarly, from Eq. (10) the following expressions for the planar potential are obtained for each case:

$$V_p^0(z)=2\pi s^{-1}[I_p(z)-\tfrac{1}{4}C\gamma^{-1}h(z)]\ , \tag{12a}$$

with

$$h(z)=\begin{cases}1-\exp(-\gamma/z^4)\\ \gamma^{-1}[1-(1+\gamma/z^4)\exp(-\gamma/z^4)]\end{cases} \tag{12b}$$

[using Eqs. (3a) and (3c), respectively],

$$V_p^+(z)=2\pi s^{-1}\{I_p(z)-\tfrac{1}{2}C\gamma^{-2}[1-(1+\gamma/z^2)\times\exp(-\gamma/z^2)]\}\ , \tag{12c}$$

$$V_p^{2+}(z)=2\pi s^{-1}\{I_p(z)-Cz^{-4}f(\gamma,z)+\tfrac{1}{3}C'\gamma'[1-\exp(-\gamma'/z^3)]\}\ , \tag{12d}$$

$$f(\gamma,z)=6z^4/\gamma^4-(6z^4/\gamma^4+6z^3/\gamma^3+3z^2/\gamma^2+z/\gamma)\exp(-\gamma/z)\ , \tag{12e}$$

and

$$I_p(z)=Z_1Z_2[A\alpha^{-2}(1+\alpha z)e^{-\alpha z}+\beta^{-1}e^{-\beta z}]\ . \tag{12f}$$

The integrals appearing in Eqs. (11) were evaluated numerically by means of a 200-point Chebyshev procedure,[28] maintaining in all cases an accuracy of 10^{-4}. We have specifically considered the Mg(0001) surface, for which

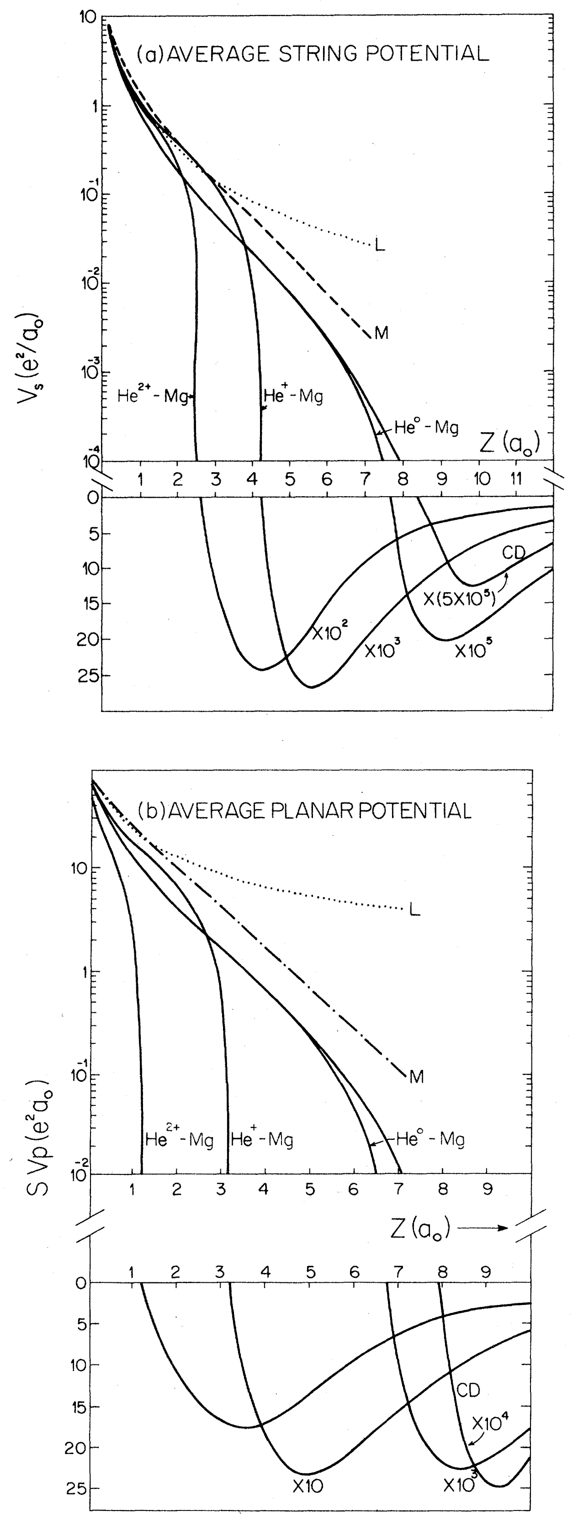

FIG. 3. Average string (a) and planar (b) potentials for the neutral, single, and doubly charged systems treated in this work (see text). Curves labeled *CD* were obtained with an alternative binary potential (see caption of Fig. 2). Also shown are the string and planar potentials constructed from the Lindhard (*L*) and Thomas-Fermi-Molière (*M*) binary potential curves, respectively. Note the changes of scale.

$s=\sqrt{3}/2d^2$ and where $d=6.05$ a.u. is the closest packing distance in the Mg-hcp structure.[29] Figures 3(a) and 3(b) show, respectively, the average string and planar potentials for the cases described above. Corresponding curves obtained for some selected universal potentials are also shown for comparison. The general trend of the curves reflects the structure of the pairwise source potential from which they are derived. Well-defined minima appear in all cases. For the neutral system, use of the binary potential given by Eq. (3a) predicts a minimum for the planar potential of -0.020 eV at a distance $z=8.3$ a.u. from the plane. However, when the binary potential accounts properly for the van der Waals minimum [Eq. (3c)], the predicted value for the depth of the planar potential well becomes -2.15×10^{-3} eV at $z=9.1$ a.u. [curve labeled *CD* in Fig. 3(b)], in better agreement with the corresponding value ($V\sim-3\times10^{-3}$ eV at $z\sim7$ a.u.) reported by authors[30,31] who have used the jellium model for the metal. This model allows for self-consistent calculation of the interaction including collective states of the metal surface, as perturbed by the presence of the projectile. The differences observed between their predictions and those reported here for the depth and position of the minimum may be attributed to differences in the approximations of the theoretical models. In our case we have the additive approximation (the use of binary gas-phase potentials to represent the interaction of the projectile with atoms in the solid) and use of only a single plane of atoms to simulate the surface. However, despite this, the surprisingly good agreement observed indicates the importance of an accurate knowledge of the van der Waals terms in the construction of a reliable surface potential for He-metal interactions, in accordance with recent reports.[32] The same general trend is observed with the string potential, as may be verified from Fig. 3(a). The minimum for the double and single charged systems appear at $z=4.2$ a.u. ($V\sim-6.7$ eV) and $z=5.6$ a.u. ($V\sim-0.73$ eV) in the string case and at $z=3.4$ a.u. ($V\sim-15.45$ eV) and $z=5.0$ a.u. ($V\sim-2.01$ eV) in the planar case, respectively.

Recent studies of Evdokimov[33] in low-energy ion scattering suggest three atoms to be the minimum number necessary to define a string, in agreement with nonempirical *ab initio* pseudopotential calculations previously reported by Cruz *et al.*[9] for interaction of helium with a string of berylium atoms. However, in the work of Evdokimov only the repulsive part of the potential is employed, and the effect of a long-range attractive term is therefore not included. In order to examine this specific effect we constructed a simple model for a plane, consisting of a regular mesh of Mg atoms, with a simple-cubic unit surface cell of side $d=6.05$ a.u. The interaction energy was calculated by direct summation of pairwise potentials between projectile and atoms in the plane (string) for different mesh (string) sizes and for *two* extreme locations of the projectile with respect to the plane, namely the *eclipsed (E)* position, referring to the projectile sitting right on top of an atom on the plane, and the *centered (C)* position, where the projectile sits in the center of the unit surface cell.

Figure 4 shows, as an example, the results of this calculation for the potential between a He^+ ion and the string

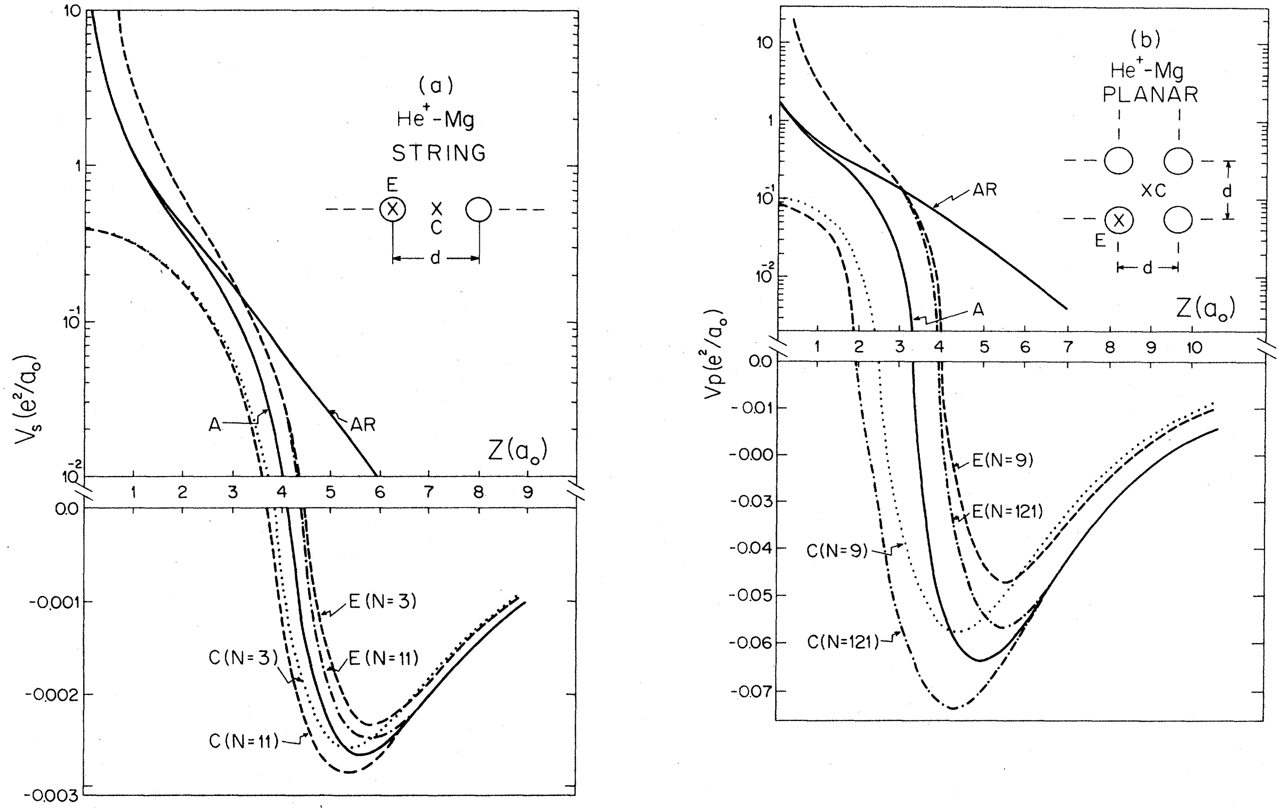

FIG. 4. (a) Potential curves for He^+ interacting with a string of Mg atoms and (b) potential curves for He^+ interacting with a plane of Mg atoms. Curves labeled E and C correspond to potentials calculated along eclipsed and centered positions, respectively, and as indicated. Convergence to the average potential (A) is achieved with $N=11$ and 121 atoms for the string and plane, respectively (see text). Curves labeled AR are the corresponding potentials constructed with the purely repulsive part of the binary interaction. Note the changes of scale.

(plane) of Mg atoms mentioned above. The corresponding average potential is also shown, for completeness. We started by defining a string with $N=3$ atoms, and then added one at a time to each extremum, calculating then the potential for various distances along the E and C positions, respectively. Similarly, a plane was constructed beginning with $N=9$ atoms. As expected, the E and C curves tend to coalesce for relatively large distances from the string (plane), yielding a unique and smooth potential curve. However, complete convergence of E and C to the average potential curve (A) is only achieved when the number of atoms is $N \geq 11$ for the string and $N \geq 121$ for the plane (increasing the number of atoms further causes negligible changes in the interaction energies). This result indicates that in this case at least 11 atoms are necessary to define the string, and 121 for the plane in order to describe properly the region around the potential well. On the other hand, a glance at the E and C curves of Figs. 4(a) and 4(b) shows that only 3 and 9 atoms are necessary to account for the repulsive region in the string and planar potentials, respectively, even with the incorporation of the attractive part of the pairwise potential. This strongly supports independent conclusions reached previously.[9,33] Finally, the curves labeled AR in Figs. 4(a) and 4(b) represent the average string (planar) potential constructed with the purely repulsive part of the binary interaction. As must be clear, the influence of the attractive part on the shape of the potential curve becomes important for distances greater than 2 a.u. for the string and 1 a.u. for the plane. Since the potential curves for the singly charged system represent an intermediate situation between the neutral and doubly charged systems, we may expect for it the same general trends as discussed above for the latter cases.

IV. CONCLUSIONS

We have calculated *ab initio* interatomic potentials for the Mg-(He,He^+,He^{2+}) systems and have shown that there exist substantial differences between these and well-known universal potentials for distances larger than about 1 a.u. The *ab initio* results also show a marked and significant dependence of the potential on the charge state of the system, which empirical potentials cannot account for. In general, the Biersack-Ziegler potential behaves properly as an average of the (He,He^+,He^{2+})-Mg curves in the repulsive region and over a wide range of internuclear distances (up to ~4 a.u.). A parametrization of the binary potentials which accurately describes the interaction for internuclear distances up to 8 a.u. has been achieved and this is expected to be valid for all distances beyond (see below).

Another *ab initio* potential for the neutral Mg-He system, restricted to the repulsive region, has also recently been described by Demetropoulos and Lawley.[10] Although the computation carried out by these authors involved a larger basis set, and a more complete CI than we have used, the good agreement between our results and theirs (see Table III) persuades us that the pseudopotential approximation and the basis set employed in our work are adequate. This, in turn, strengthens our confidence in the quality of the profiles of the potentials obtained for the ionic systems, although a single-state curve had to be considered in the study of the $(\text{Mg-He})^+$ case, due to the strong Rydbergization of the Mg excited states, and also for the $(\text{Mg-He})^{2+}$ case, where an avoided crossing appears for internuclear distances between 6.0 and 9.0 a.u. In agreement with Chiles and Dykstra,[23] we find no potential minimum for the neutral system in the region up to 8.0 a.u. On the other hand, for the ionic systems we find well-defined minima for distances below 7.0 a.u.

The van der Waals minimum reported by Chiles and Dykstra for the neutral system falls outside the range of our calculations. It is reasonably predicted, however, by our corresponding parametrized curve, thereby giving confidence in the adequacy of the suggested parametrization of the binary curves. Nevertheless, in order to include this minimum properly in our calculations, an alternative parametrization has been proposed.

The parametrized potentials described were used to construct average potentials for the He^0, He^+, and He^{2+} systems interacting with both a string and plane of Mg atoms. It was found, of course, that the effect of the long-range part of the binary potential is crucial in determining the minimum number of atoms needed to define a string and plane at relatively large distances. For short distances the effect of long-range terms may for all practical purposes be neglected, and 3 or 9 atoms are sufficient to define the string or plane, regardless of the ionic state of the system.

It is interesting to note that superposition of binary gas-phase potentials even appears to be a rather good approximation for the study of atom-metal surface interactions, provided that the long-range terms in the binary potential are accurately known. In the case of the He-Mg interaction, for example, we included the van der Waals minimum of Chiles and Dykstra, in the He-Mg surface potential, obtaining good agreement with jellium calculations. It is well known that the pairwise sum method is a fairly well justified approach for collisions which probe the highly repulsive wall of the binary potential, as is the case in keV-ion surface scattering.[34] However, for thermal-atom surface scattering studies,[35] where the long-range part is very important, this method is only a rough approximation. The projectile interacts simultaneously with several surface and near-surface (bulk) atoms and important collective (many-body) effects appear,[36] particularly for atom-metal surface interactions, where the polarization forces play an important role. In contrast to the atom-metal case, a sum of pairwise terms is more generally accepted in atom-insulating material surface interaction studies, due to the more localized electronic clouds (tight-binding approximation). We stress at this point that no many-body terms have been taken into account in the work we have described. Whilst these could be of a relatively minor importance in the neutral case, for the ionic interactions they could well play a major role since there is already evidence[37] that large nonadditive effects are present for small ionic systems.

Work currently in progress aims at accounting for many-body contributions to the He-Mg surface potential, from an *ab initio* point of view. Several planes of atoms are introduced and a realistic structure for the corresponding Mg surface is employed.

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