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# Repulsive interatomic potentials calculated using Hartree–Fock and density-functional theory methods

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## Abstract

The repulsive part of the interatomic potential affects the outcome of computer simulations of many irradiation processes of practical interest, like sputtering and ion irradiation range distributions. The accuracy of repulsive potentials is studied by comparing potentials calculated using commonly available density-functional theory (DFT) and Hartree–Fock (HF) methods to highly accurate fully numerical HF and Hartree–Fock–Slater (HFS) calculations. We find that DFT calculations utilizing numerical basis sets and HF calculations using *decontracted* standard basis sets provide repulsive potentials which are significantly improved compared to the standard universal ZBL potential. The accuracy of the calculated potentials is almost totally governed by the quality of the one-particle basis set. The use of reliable repulsive potentials open up new avenues for analysis of ion irradiation experiments. © 1997 Elsevier Science B.V.

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## 1. Introduction

The slowing down of energetic ions in materials is conventionally described by two different phenomena: elastic collisions of the energetic ion with atoms in the sample and collisions of the ion with electrons. The former process, also called nuclear slowing down, dominates at low energies ( $E_{\text{kin}} \lesssim 1$  keV/amu), whereas the latter, electronic slowing down, dominates completely at high energies.

Nowadays, binary collision approximation (BCA) [1,2] or molecular dynamics (MD) [3,4] computer simulations can be used to describe the entire slowing down process of an energetic ion and the resulting collision cascade. The atomic collisions are in both methods described as a classical scattering process with an interatomic potential acting between the atoms. In treating processes where the atoms collide at kinetic energies of the order of 1 eV/amu–1 keV/amu, it is particularly important to know the repulsive part of the interatomic potential accurately.

Several previous studies have probed the effect of the repulsive potential on the outcome of simulations of collision processes. Calculation of ion depth distributions has shown that the strength

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of the repulsive potential is directly reflected on the distribution of implanted ions and thus primary damage [5]. Sputtering yields [6] and lifetimes of excited nuclear energy levels obtained from simulations of slowing down of energetic nuclei [7] have also been found to be sensitive to the form of the atom–ion interaction. On the other hand, the number of point defects produced in collision cascades in silicon has been shown to be largely independent of the choice of a repulsive potential [8]. Since local melting and crystal regeneration is even more pronounced in typical metals than in Si [9], one can expect the repulsive potential to have even less effect on damage production in them. It appears that in physical problems where the outcome is determined by energetic collisions between atoms, rather than the local melting in collision cascades, the exact form of the repulsive potential is significant.

Depth distributions of implanted ions can be measured to a high accuracy using several different characterization techniques, like secondary ion mass spectroscopy (SIMS), nuclear resonance broadening (NRB) and elastic recoil detection analysis (ERDA) [10–12]. Provided that the repulsive potential acting between atoms is known with an accuracy comparable to the experimental accuracy of these methods, it is possible to analyze other parameters affecting the experiment – like the sample structure or electronic slowing down – using MD or BCA simulations of the range profiles [13,14]. Therefore, there is a clear need to know the accuracy of repulsive potentials used in simulations.

It is quite difficult to measure the repulsive interaction directly. Although numerous measurements have probed the repulsive part of the potential *well* [15], very few studies have attempted to measure the part between about 10 eV and 100 keV of interest here. Kirchner et al. [16] studied the platinum–oxygen potential both experimentally and theoretically up to energies of 80 eV. Lane and Everhart [17] measured the repulsive potentials of several noble gas systems at kilo-electron-volt energies.

Loftager, Hartung and co-workers have studied repulsive potentials by measuring scattering cross sections of several ions in noble-gas targets in the

energy range 2.5–400 keV [18–20], although they do not derive the actual repulsive potential from their data. They report that the experimental scattering cross sections can be fairly well reproduced by integrating a theoretical repulsive potential, even though inelastic energy loss also occurs during the collision process. This observation further emphasizes the importance of the repulsive potential.

Unfortunately the uncertainties of the experimental repulsive potentials mentioned above are of the order of 10% or more, and may contain systematic errors of unknown magnitude due to electronic excitation effects. Hence they are not accurate enough for the purposes of the present study, where we will examine considerably smaller differences between calculated potentials. We did, however, compare theoretical potentials calculated with the density-functional theory (DFT)/DMol method (see below) with the He–He and He–Ne potentials of Ref. [17], and found the theoretical and experimental potentials to be in agreement within the experimental uncertainty of 20%.

Many different theoretical methods have been used to determine repulsive interatomic potentials [2,6,15,16,20–22]. A much used method has been an approximate quantum mechanical method first presented by Gombas [23,24]. Although potentials calculated with this method appear to provide a good approximation of the real potential over the whole repulsive interaction range, comparison with more realistic calculations have shown that they can be off by 20% for certain radial separations [2,25].

Perhaps the most used potential is the universal repulsive potential by Ziegler, Biersack and Littmark (ZBL) [2], which is an analytical potential that can be easily evaluated for any atom pair. It has been constructed by fitting an analytical function to a large number of repulsive potentials evaluated with the Gombas approximate method for different pairs. The fit has a standard deviation of 18% from the Gombas-type potentials.

The wide availability of both research and commercial quantum mechanical ab initio software has made it both easy and increasingly common to determine specific repulsive potentials for the ion pair of interest using ab initio methods (see e.g. Refs. [5,6,20,25–27]). Most studies, however, have

calculated the potential using only one quantum mechanical method, which makes it hard to deduce whether any systematic errors may be present in the results. Since almost all ab initio methods have been originally designed to describe chemical or solid-state processes near equilibrium, it is not clear whether they can be used for the specialized problem of calculating the energy of diatomics at very close separations.

In the present work we want to study the accuracy of repulsive potentials obtained with different quantum mechanical approaches. We are not aware of any previous study where such a methodological study of repulsive potentials obtained with modern calculation methods would have been made.

The repulsive potentials are calculated using standard DFT and Hartree-Fock (HF) ab initio programs. These potentials, obtained with methods relying on basis set expansions, are compared to results obtained using numerical HF and Hartree-Fock-Slater (HFS) methods. Since the numerical methods do not assume any global form for the basis functions, they provide a highly accurate standard for the energies to which the other potentials can be compared. Eckstein et al. [6] have previously used a fully numerical HFS method to obtain the repulsive potential for Si-Si. They did not, however, perform any comparison with potentials obtained using other ab initio methods. We also include the widely used ZBL universal repulsive potential in this study in order to examine its accuracy. The four diatomics C-C, H-Si, N-Si and Si-Si are chosen as model systems. Since an accurate treatment of heavy atoms would require the consideration of relativistic effects, no heavy atoms have been included.

For Si Si we performed a more detailed study on both the effects of electron correlation as well as basis set convergence. The Si-Si repulsive potential is also calibrated using a fully numerical HF method [28,29].

## 2. Potential calculations

The interatomic potential  $V(R)$  acting between two atoms is here defined as the difference between

the total energy at an interatomic distance  $R$  and the total energy of the isolated atoms

$$V(R) = E(R) - E(\infty). \quad (1)$$

By the repulsive potential, we simply mean the part of the total potential at small internuclear separations  $R$  where  $V(R) > 0$ .

In a crystal, a diatomic potential does of course not accurately describe the interatomic potential functions. In studies of H atoms surrounded by Cu atoms, however, the first author has found that the diatomic potential does not differ much from a bulk potential at energies  $\gtrsim 10$  eV [30]. Furthermore, in collision cascade calculations where the low-energy part of the potential is relevant, the repulsive potential is usually fitted to some many-body potential which describes the low-energy interactions [31], whence the low-energy part of the diatomic repulsive potential loses its significance.

The repulsive potentials are here calculated using several computational approaches. The fully numerical two-dimensional (2D) HFS method [28,29] is used for providing accurate reference potentials for the DFT and the HF calculations. For Si-Si, the HF limit is determined by fully numerical HF calculations. The effect of electron correlation has been studied at the second-order Møller-Plesset perturbation theory level (MP2) [32] and at the coupled-cluster singles and doubles level augmented by a perturbative correction for triple excitations (CCSD(T)) [33,34].

The interatomic potential  $V(R)$  is obtained by calculating the total energy of the diatomic system at different interatomic separations  $R$ . In the comparison of the potentials, only a few distances  $R$  are used, while to obtain the potentials for actual simulations the potential is calculated at denser  $R$  intervals.

For practical BCA and MD simulations, many authors fit the parameters to some analytical function (e.g. the ZBL potential) for the repulsive potential data [22,6]. However, even if a large number (eight for the ZBL potential) of free parameters are used, we have found it very difficult to obtain a good fit to the strongly decreasing potentials over a large energy range (between 1 eV and 100 keV). Typically, the fits result in errors in the potential energy or its derivative of the order of

5–10% in some part of the fitting regime. To prevent the introduction of unnecessary fitting errors in our simulations, we use spline interpolation [35] over dense  $R$  intervals (typically,  $\Delta R \sim 0.02$  Å) of the potential data to obtain  $V(R)$  at a given  $R$ .

### 2.1. Density-functional theory calculations

The DFT at the local-density approximation (LDA) level is widely used in the research community due to its relatively good accuracy and low computational cost for large numbers of atoms [36–38]. In the DFT approach, the Kohn–Sham (KS) equations

$$\left[ \frac{-\hbar^2}{2m} \nabla^2 + V_s(r) + V_{xc}(r) \right] \phi_i(r) = \varepsilon_i \phi_i(r), \quad (2)$$

$$\rho(r) = \sum_i |\phi_i(r)|^2, \quad (3)$$

$$V_{xc} = \frac{d(\rho \varepsilon_{xc})}{d\rho} \quad (4)$$

are self-consistently solved. In (2),  $V_s$  is the electrostatic potential due to nuclei and the electron charge distribution, and  $V_{xc}$  is the exchange and correlation term.

The molecular orbitals  $\phi$  are expanded as a linear combination of atomic orbitals,

$$\phi_i(r) = \sum_j c_{i,j} \chi_j(r). \quad (5)$$

The standard basis sets ( $\chi_j$ ) used in the DMol [39] DFT/LDA package [37,40] consist of two numerically tabulated atomic basis functions for each occupied atomic orbital. These are generated by solving the atomic DFT equations once for the neutral atom and once for the doubly charged cation. Delley [37] prefers to call them “double numerical basis sets” (DN) to be contrasted with double-zeta (DZ) basis, where the radial functions possess an analytical form. The DMol method is not fully numerical since the atomic orbitals are kept fixed during the calculation while all the integrals are computed numerically. In our DMol calculations, we used the Vosko–Wilk–Nusair Hamiltonian with no gradient corrections. Use of

different exchange and correlation functionals, including gradient corrections, was not found to affect the results significantly. This level of theory has previously been used to determine repulsive potentials [5,41].

Since the integrals are computed numerically, DMol can use any type of normalizable function which satisfies regularity condition for molecular orbitals. Delley [37] uses two types of orbitals to improve on the accuracy of the standard DN basis sets; numerical orbitals of positive ions, and orbitals of hydrogenic atoms with a specified nuclear charge. We examined how both kinds of orbitals affected the atomic energies at close separations. Adding additional cationic basis functions was found to affect the energy convergence rather slowly. Adding hydrogenic orbitals, however, had a remarkably strong effect on the energies obtained at close separations.

As an example case we discuss in detail results of two Si atoms at a separation of 0.0360795 Å. Tests at other atomic separations and cases have been found to give similar results. Using just the standard Si and  $\text{Si}^{2+}$  orbitals gave  $V(R) = 63\,281$  eV, to be compared with the value 58 829 eV obtained from 2D calculations. Adding cationic orbitals for  $\text{Si}^{2+}$  with the 3s electrons removed reduced the energy to 63 178 eV, and further adding orbitals for  $\text{Si}^+$  with a 3p electron removed reduced the energy only to 63 091 eV. On the other hand, adding 1s, 2p, 3d and 4f hydrogenic orbitals for  $Z = 14$  to the standard basis reduced the energy to 60 846 eV, and further adding the same hydrogenic orbitals for atoms with  $Z = 13, 11$  and 15 reduced the energy to 59 050 eV (since each orbital is orthogonalized against the previous ones, the order in which orbitals are added can affect the results slightly). This result agrees much better with the 2D result than the value obtained with the unmodified DN-type basis set.

In, practice, the addition of orbitals to the basis set is achieved by constructing a new basis set with the “DATOM” utility supplied with the DMol program package, and choosing the “user-defined” basis option for the DMol run. For elements with  $Z < 11$  the standard basis sets provided with the program package are already augmented with hydrogenic orbitals. For the final C–C diatom

calculations we used this standard basis set. For the diatoms involving Si we used a basis set where the Si DN basis was extended with the hydrogenic orbitals for  $Z = 14, 13, 11$  and  $15$ , each containing the  $1s, 2p, 3d$  and  $4f$  hydrogenic orbitals. Although these basis sets were found to give quite sufficient accuracy in the repulsive potential, tests of larger basis sets for C–C and Si–Si for a few  $R$  values gave even better agreement with the 2D results.

## 2.2. Numerical Hartree–Fock–Slater Calculations

The fully numerical 2D HFS method has recently been described in detail [28,29] and only a short description will be presented here. The 2D program is also available on the World Wide Web [29].

For diatomic molecules, the orbitals can be expressed in elliptical coordinates as

$$\phi_a(\eta, \xi, \varphi) = f_a(\eta, \xi) e^{im_a\varphi}, \quad (6)$$

where  $\eta, \xi$  and  $\varphi$  are the prolate spheroidal coordinates defined as with the centers located at  $z_1 = -R/2$  and  $z_2 = R/2$  along the  $z$ -axis,  $R$  being the internuclear separation. The angular part ( $\varphi$ ) can be treated analytically. A similar ansatz can also be written for the electron-interaction potential which is obtained by solving the Poisson equation. In the HFS approximation, the  $V_{xc}$  potential in (2) consists of a local statistical exchange potential [42]

$$V_{xc}(r) = -3\alpha(3\rho(r)/8\pi)^{1/3}, \quad (7)$$

where  $\rho$  is the total electron density and  $\alpha = 0.7$  is a constant.

The two-dimensional “radial” part of the orbitals and potentials are discretized and the HFS and Poisson equations are solved using a two-dimensional numerical approach. The discretization is performed using an eighth-order central difference stencil on a two-dimensional grid (or subgrids) and the resulting large and sparse system of linear equations is solved by the (multicolor) successive overrelaxation method [43]. Since the numerical HFS energies do not suffer from any significant basis set truncation errors, they are used as reference potentials for the basis set calculations.

## 2.3. Hartree–Fock calculations

In the previously described methods the total density was chosen as the fundamental variable, which by applying the variational principle to the Schrödinger equation leads to the KS equations. In order to solve these equations one has to assume the form of  $V_{xc}$ . In the HF method the total wave function is described by a Slater determinant. By applying the variational principle, with this wave function as the fundamental variable, the HF equations are obtained. The HF equations are similar to (2) except that  $V_{xc}$  is replaced by the HF exchange operator

$$K_j(1)\phi_i(1) = \int \left[ \phi_j^*(2) \frac{1}{r_{12}} \phi_i(2) dx_2 \right] \phi_j(1). \quad (8)$$

In practice the molecular orbitals,  $\phi_i$ , are expanded in Gaussian basis functions. As virtually all standard basis sets are developed for optimal performance in describing chemical phenomena, it is not obvious that their functionality can be extended to describe the strongly repulsive part of the interaction potentials. In addition to basis set studies at HF level, we estimated the contribution from electron correlation by performing MP2 and CCSD(T) calculations on the Si–Si system. The HF and MP2 calculations were performed with the TURBOMOLE program package [44] and the CCSD(T) calculations with the ACES II program package [45] using decontracted valence-triple zeta basis sets [46]. To assess the basis set truncation errors of the HF calculations we performed numerical HF calculations on Si–Si.

All the HFS, DMol, and HF calculations on the different diatoms were done on the  $\Sigma$ -state with the lowest spin multiplicity. The numerical and Gaussian basis set calculations were performed with the equilibrium electron configuration for all internuclear distances.

## 3. Results and discussion

At short distances the interaction energy is dominated by the nuclear–nuclear repulsion potential. Since this dominant contribution is independent of the model, it makes it hard to

distinguish the differences between different methods. In order to pronounce the differences in the studied methods, we present our results in terms of the screening function and the electronic interaction energy. The screening function is defined by

$$V(R) = \frac{Z_1 Z_2 e^2}{R} \Phi(R), \quad (9)$$

where  $V(R)$  is the interatomic potential,  $Z_1$  and  $Z_2$  are the nuclear charges, and  $R$  is the internuclear distance. At long distances  $\Phi(R)$  vanishes, and for very short distances there is almost no screening of the nuclear–nuclear interaction and  $\Phi(R)$  approaches one.

A transparent comparison of the different computational approaches is obtained by comparing the electronic contribution to the repulsion potential. The electronic interaction energy is calculated as

$$E_{\text{el}}^{\text{inter}} = E_{\text{el}}^{\text{diatom}} - E_{\text{atom } 1} - E_{\text{atom } 2}, \quad (10)$$

where  $E_{\text{el}}^{\text{inter}}$  is the electronic contribution to the interaction energy,  $E_{\text{el}}^{\text{diatom}}$  the electronic contribution to the energy of the diatom, and  $E_{\text{atom } 1}$  and  $E_{\text{atom } 2}$  are the total energies of the two atoms.  $E_{\text{el}}^{\text{inter}}$  is related to  $V(R)$  by

$$V(R) = E_{\text{el}}^{\text{inter}} + \frac{Z_1 Z_2 e^2}{R}. \quad (11)$$

At very small  $R$  values the nuclear interaction dominates and the  $E_{\text{el}}^{\text{inter}}$  contribution to the total potential will not be significant. At somewhat larger  $R$  values (smaller interaction energies),  $E_{\text{el}}^{\text{inter}}$  and the nuclear potential will be of the same order of magnitude, but of opposite sign. Because of this, a difference in  $E_{\text{el}}^{\text{inter}}$  can in some cases be reflected in a larger change in the repulsive potential.

To give an idea of how deviations in  $E_{\text{el}}^{\text{inter}}$  are reflected in  $V(R)$ , we give the maximum difference between the DFT, HF, and ZBL potentials and the HFS potential for interaction energies above 1 keV. At lower interaction energies, comparing repulsive potentials with a ratio is not very instructive because of the singularity at the potential zero-crossover.

There are three major sources of discrepancies in the results obtained with the studied methods. These are the different treatment of exchange, the

size of the one-particle space (basis set), and the effect of electron correlation.

In order to study the effects of the different exchange terms in DFT and HF approaches, we compared the repulsive potential for Si–Si obtained from numerical HFS and HF calculations. These numerical calculations are free from basis set truncation errors. For interaction energies above 1 keV the maximum deviation in  $V(R)$  is only 0.25%, which clearly shows that the effects due to different exchange terms are negligible.

The effect of the limited basis sets was studied by comparing results obtained from DMol and HF calculations to numerical HFS and HF results.

The basis set truncation errors (BSTE) of the DMol calculations on Si–Si were estimated by combining numerical HFS and Gaussian basis set DFT calculations with the corresponding DMol DFT results. This comparison showed that the BSTE of the DMol calculations on Si–Si are less than 1.0% of the repulsive potential above 1 keV. The BSTE grows monotonically as the distance becomes shorter. Since the numerical HFS calculations are performed with fixed occupation numbers while in the DMol calculations they are optimized, the basis set truncation error of the DMol energies is somewhat compensated. For Si–Si, this relaxation contribution improves the agreement with the numerical results and corresponds to less than 1.3% of the repulsive potential.

The HF method provided relatively accurate potentials already with standard DZ basis sets. For very short internuclear distances the heavy contraction of the “core-like” basis functions resulted in larger deviations. Additional flexibility was obtained by decontracting the DZ basis sets, which resulted in a much better agreement with 2D HFS results over the whole distance range.

For Si–Si, the basis set dependence was further investigated by performing numerical 2D HF calculations. The fully numerical HF and HFS potentials differ at most by 0.8 au (22 eV) which corresponds to 0.25% of the repulsive potential above 1 keV. For Si–Si, the BSTE of the basis set calculations using decontracted DZ quality basis set are less than 7.5%. Calculations using decontracted basis sets of valence-triple zeta quality augmented with one polarization function (TZVP)

provide potentials which possess BSTE of about 5.5%. Since the HF energy for short internuclear distances converges slowly with the size of the atom-centered basis set it is necessary to add basis functions between the nuclei (bond functions) to obtain very accurate repulsion potentials.

We compared also the LDA and HF results obtained with decontracted Gaussian basis sets of DZ and TZVP quality. For Si–Si interaction energies above 1 keV the maximum deviations obtained with DZ basis sets are 5.5% and 7.4% for LDA and HF, respectively. For decontracted TZVP basis sets the corresponding deviations are 5.0% and 5.5%. For both methods the BSTE is rather constant over the whole distance range, resulting only in a shift of the potential curve. This indicates that the derivative of the potential should be of much better quality.

Thus we can conclude from these basis set studies that for decontracted Gaussian DZ basis sets the LDA results are somewhat better than the HF results, but both methods suffer from the poor convergence of Gaussian basis sets towards the basis set limit. We found also that the numerical basis sets used in the DMol calculations are superior to Gaussian basis sets, except at very high energies.

The effect of electron correlation was studied by performing MP2 and CCSD(T) calculations on Si–Si. The MP2 correction to the interaction energy was found to be only about 3–5 eV over the whole distance range and as judged from coupled-cluster results the correlation contribution is less than 0.1% of the repulsive potential above 1 keV.

Thus we can state that the accuracy of the calculated repulsive potential is almost totally governed by the quality of the one-particle basis set, whereas the effects arising from the use of different computational methods are significantly smaller.

The results of the electronic structure calculations are illustrated in Figs. 1 and 2. In Fig. 1 the potentials are compared by plotting the  $E_{\text{el}}^{\text{inter}}$  ratios between the DFT, HF, and ZBL potentials to the 2D HFS potential. In Fig. 2, the screening functions  $\Phi(R)$  of the four diatoms are shown. The comparison of the  $E_{\text{el}}^{\text{inter}}$  values offers the best illustration of the differences between the electronic structure calculations, while the comparison of the screening functions  $\Phi(R)$  shows how these

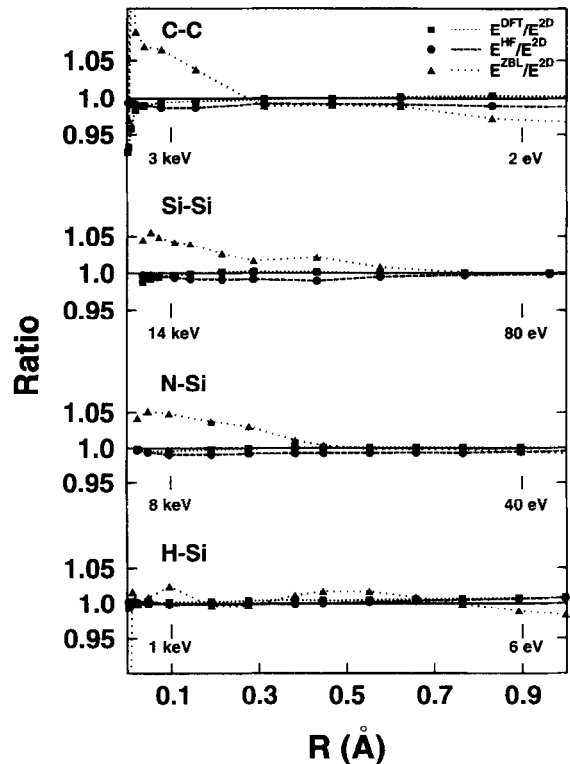


Fig. 1. Ratios between the electronic contributions  $E_{\text{el}}^{\text{inter}}$  to the repulsive potentials. DFT denotes the DMol density-functional calculations, HF the Hartree-Fock method and ZBL the commonly used ZBL universal repulsive potential. The 2D HFS potential is used as a standard to which the other potentials are compared. The energy values within the figure show the approximate actual strength of the calculated total repulsive potential  $V(R)$  at  $R = 0.1$  and  $0.9 \text{ \AA}$  for each diatom.

differences will be reflected in practical calculations of radiation effects.

For  $V(R) > 1 \text{ keV}$  the agreement between the DMol DFT and 2D HFS electronic interaction energies is within 2%, with the exception of C–C where the discrepancy grows to 9.5% for  $R < 0.02 \text{ \AA}$ . However, since at these separations the nuclear part dominates completely, the deviations are not reflected in the final potential. This is evident in Fig. 2, where practically no difference between the DFT and HFS results can be seen. The difference in the potential energies above 1 keV is less than 0.7% for all atom pairs.

For  $E_{\text{el}}^{\text{inter}}$  the agreement between 2D HFS results and results obtained with HF using decon-

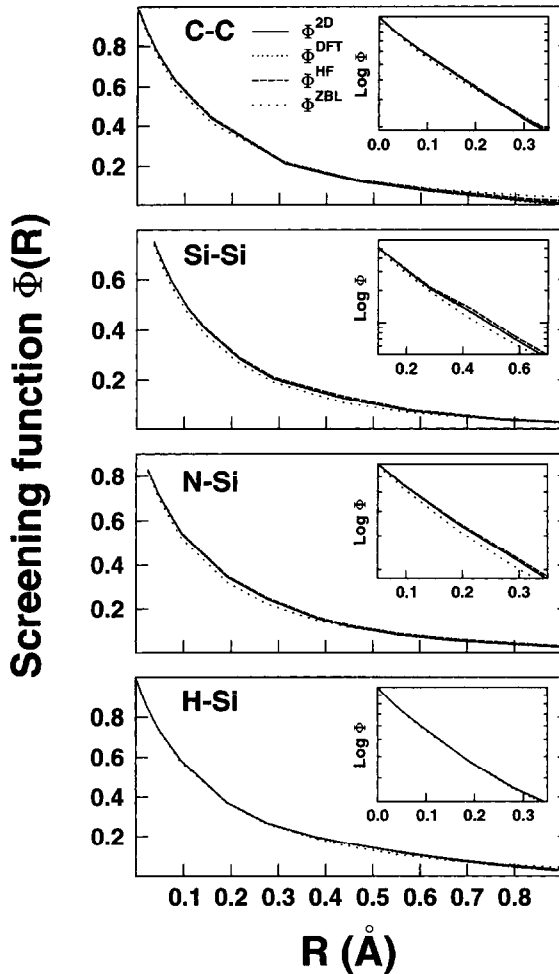


Fig. 2. Screening functions for the four diatoms. Labels are as in Fig. 1. The insets show the part of the screening function where the potential  $V(R)$  is larger than roughly 0.5 keV.

tracted DZ basis sets is within 1.4% for all pairs. The deviations in the interaction potential  $V(R)$  are larger than for DMol, ranging from 0.2% to 7.4%.

In Fig. 1, particularly for C–C, the earlier mentioned systematic shift of the HF curve can be seen. As a similar shift could be found for LDA results using Gaussian functions, it must be due to the poor convergence of the Gaussian basis sets at short bond distances.

Above 1 keV the maximum differences in the potential energies between DMol and 2D HFS results are 0.6% for C–C and Si–Si, and 0.4% for H–

Si and N–Si. The corresponding differences between the HF and 2D HFS interaction potentials are 3.1% for C–C, 7.4% for Si–Si, 3.9% for N–Si and 0.2% for H–Si.

Considering its nature as an average potential, it is not surprising that the ZBL universal repulsive potential differs in all cases from the HFS results. The maximum difference between the ZBL and HFS electronic interaction energies and interaction potentials is 14.7%. The difference emphasizes the fact that the ZBL potential is not suitable for applications in which high accuracy is desired in the description of atomic collisions. The deviations in  $E_{\text{el}}^{\text{inter}}$  are also visible as  $\Phi$  differences in Fig. 2.

Several previous studies have found that differences in repulsive potentials can result in significant changes in simulation results. A relative difference in repulsive potentials has been found to be reflected in a relative change of about the same magnitude in implantation range profiles [5,12,14,47]. Eckstein et al. [6] have shown that the effect of the choice of the repulsive potential can be even greater on sputtering results.

Since the previous studies already have dealt in detail with the effect of potentials on simulation results, we only illustrate the differences with one example in the present context. We calculate the range distribution of 40 keV N implantation in Si using the MDRANGE program [47,48] for the DMol and ZBL interatomic potentials (the DMol DFT rather than the HFS 2D program was used because a potential calculated at dense intervals was available from a previous study [12]). To prevent channeling effects, an 8° tilt of the sample is used. The electronic slowing down, obtained from the SRIM96 computer code [49], contributed about 50% to the slowing down.

The mean ranges of the distributions differ by 7%, which reflects well the 9% root-mean-square difference between the potentials in the 20 eV–20 keV energy range (see Fig. 3).

Recent studies have demonstrated that by assuming that the repulsive potentials are accurate, one can deduce the electronic stopping power or make conclusions about the sample structure by comparing simulated and experimental range profiles [12–14]. Such studies rely completely on the accuracy of the interatomic potential. For in-



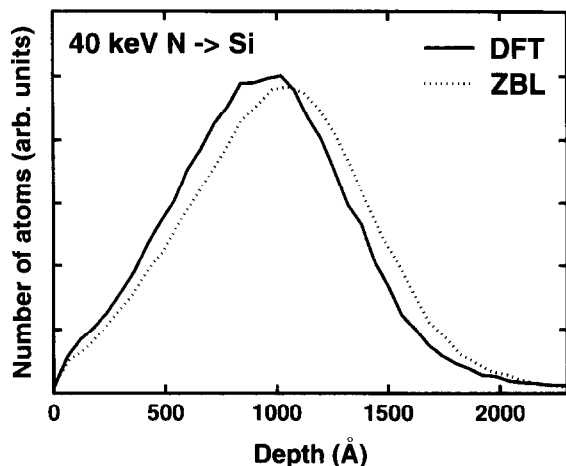


Fig. 3. Range distributions of 40 keV N implantation of Si calculated using the MD Range calculation method for the DMol DFT and ZBL interatomic repulsive potentials.

stance, in stopping power studies in which the first author participated [12,14] use of the ZBL interatomic potential would have caused deduced electronic stopping powers to differ roughly 5–10% from those obtained with DMol potentials. Studies of sample structure would not be meaningful without a repulsive potential of roughly 1% accuracy [13].

#### 4. Conclusions

In this paper, fully numerical HFS and HF methods to calculate accurate repulsive potentials have been used to study the accuracy of the repulsive potentials for H–Si, N–Si, Si–Si and C–C obtained using commonly available ab initio codes. We found that standard basis set methods can be used to calculate accurate repulsive potentials, provided that the basis sets have *enough flexibility* close to the core. In fact, the accuracy of the calculated potentials is totally dependent on the quality of the basis sets, whereas the ab initio level of theory has an almost negligible effect. We also found that it is very difficult to reach the basis set limits by using Gaussian functions. This problem in the strongly repulsive region is independent of the methods used. To obtain very accurate potentials

using Gaussian functions, bond functions have to be added to the basis sets.

We found that the DMol DFT method utilizing numerical basis functions can be used to obtain repulsive interatomic potentials for H–Si, N–Si, Si–Si and C–C with an accuracy of the order of 1% provided that the numerical basis sets contain hydrogenic basis functions. If new repulsive potentials are calculated by any of the standard basis set methods considered here, it is strongly advised to calculate a few reference points by a fully numerical approach.

Finally, we discussed how the accurate interatomic potentials enable more extensive studies of less well-known parameters of irradiation experiments, like the electronic slowing down and sample structure.

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