Comments

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Comment on "Pseudopotentials that work: From H to Pu"

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In this Comment we report on small differences found in the ion-core pseudopotentials of Si between our results and the values tabulated earlier by Bachelet, Hamann, and Schlüter. It is shown that the rounding of the parameters in their tables leads to inaccuracies. For convenience to future users of the Bachelet-Hamann-Schlüter potentials a correct set of reference tables is given.

The introduction of norm-conserving ion-core pseudopotentials[1,2] has been an important development in pseudopotential theory. These pseudopotentials are transferable by construction. Therefore if one accepts the underlying exchange and correlation functional, they may be used in calculations involving the electronic properties of atoms, molecules, surfaces, and solids. The set of ion-core pseudopotentials for the elements of hydrogen to plutonium have been tabulated by Bachelet, Hamann, and Schlüter (hereafter denoted by BHS).[3] Using the tables of BHS, calculations of electronic properties have been performed by several groups.

The ion-core pseudopotentials of BHS, $\Delta V_l^{\rm ion}(r)$, may be considered to be very useful because of the fact that they are expanded in terms of error functions and Gaussians, with expansion coefficients A_i [given in Eq. (2.22) of the BHS paper] making it possible to obtain analytical expressions for matrix elements not only for Gaussian basis functions but also for a basis set of plane waves.[4] However, as stated in the BHS paper, the fitting coefficients A_i can take on rather large values. Since BHS considered it not practical to tabulate numbers with too many digits, these coefficients A_i were transformed to new coefficients C_i by means of an orthogonality transformation. The triangular matrix Q of this transformation is given in closed form in Eq. (2.26) of the BHS paper. According to BHS the advantage of this transformation is that an accuracy of four digits in the C_i coefficients suffices to calculate the ion-core pseudopotentials $\Delta V_l^{\rm ion}(r)$. The C_i coefficients are given in Table IV of the BHS paper. From these tabulated values the A_i's and subsequently the pseudopotentials $\Delta V_l^{\rm ion}(r)$ are obtained by applying the inverse orthogonalization procedure.

Finally, in order to allow users to check the accuracy of their programs and their own inverse orthogonalization procedures, BHS list in Table V of their article the $l=0,1,2$ pseudopotential of Si. All the calculations in the BHS paper have been performed in single precision on a Cray-1 computer, i.e., using 64-bit arithmetic.

In comparing the results of calculations performed independently by the present authors with Table V of Ref. 3, small differences were found in $\Delta V_l^{\rm ion}(r)$ of Si for r close to zero. The deviations are of the order 0.5% at small r and decrease rapidly with increasing r. Although the discrepancies are small they nevertheless introduce some doubt about the accuracy of the programs.

Upon investigation of this problem, we found that seemingly trivial details in the computational procedures as well as the precision of various computers made the conversion from the coefficients C_i to A_i ambiguous. The small changes in the ion-core pseudopotential are due to numerical inaccuracies in the computation of the overlap matrix S, the transfer matrix Q and the inverse orthogonality transformation, given respectively by Eqs. (2.27), (2.26), and (2.28) of Ref. 3.

The overlap matrix S can be calculated analytically in terms of the tabulated parameters α_i, and it is easily shown that the rounding of these parameters allows the determination of the matrix elements of S with a relative accuracy of the order of 0.1%. However, the transfer matrix Q is rather sensitive to the errors in the overlap matrix. The uncertainty in the matrix elements $Q_{i,j}$ is of the order of the uncertainty in $S_{i,j}$ for $i=1$, but it drasti-

TABLE I. Silicon ion-core pseudopotential for $l=0$ on a real space mesh, as derived from the coefficients in Table IV of Ref. 3, obtained on a Control Data Corporation Cyber 205 computer (128 bits), on a Digital Equipment Corporation VAX11/780 computer (64 bits), and on a Burroughs B7900 computer with 96-bit variables, compared to Table V of Ref. 3. All data are in hartree atomic units.

R	$\Delta V_l^{\text{ion}}(r)$ from Table V of Ref. 3	$\Delta V_l^{\text{ion}}(r)$ calculated from Table IV of Ref. 3
0.0	2.2360	2.2374
0.1	2.1929	2.1942
0.2	2.0610	2.0616
0.3	1.8327	1.8327
0.4	1.5002	1.5000
0.5	1.0598	1.0598
0.6	0.5170	0.5172
0.7	−0.1078	−0.1075
0.8	−0.7729	−0.7727
0.9	−1.4175	−1.4175
1.0	−1.9743	−1.9744
1.1	−2.3894	−2.3895
1.2	−2.6395	−2.6395
1.3	−2.7354	−2.7354
1.4	−2.7133	−2.7133
1.5	−2.6181	−2.6181
1.6	−2.4893	−2.4894
1.7	−2.3534	−2.3536
1.8	−2.2245	−2.2246
1.9	−2.1071	−2.1073
2.0	−2.0016	−2.0017
2.1	−1.9062	−1.9063
2.2	−1.8196	−1.8197
2.3	−1.7403	−1.7404
2.4	−1.6676	−1.6677
2.5	−1.6007	−1.6007

TABLE II. Silicon $l=0$, 1, and 2 ion-core pseudopotentials $\Delta V_l^{\text{ion}}(r)$ on a real space mesh as derived from the coefficients in Table IV of Ref. 3. All data are in hartree atomic units.

R	$l=0$	$l=1$	$l=2$
0.0	2.237 449	−2.480 696	−4.669 536
0.1	2.194 211	−2.485 788	−4.720 311
0.2	2.061 617	−2.500 993	−4.856 036
0.3	1.832 669	−2.525 832	−5.037 463
0.4	1.499 964	−2.558 844	−5.224 481
0.5	1.059 806	−2.597 160	−5.389 462
0.6	0.517 183	−2.636 615	−5.512 217
0.7	−0.107 506	−2.672 411	−5.565 668
0.8	−0.772 737	−2.700 025	−5.510 829
0.9	−1.417 522	−2.715 882	−5.310 641
1.0	−1.974 392	−2.717 591	−4.954 168
1.1	−2.389 533	−2.703 776	−4.472 291
1.2	−2.639 498	−2.673 775	−3.931 942
1.3	−2.735 361	−2.627 513	−3.411 624
1.4	−2.713 267	−2.565 597	−2.973 033
1.5	−2.618 140	−2.489 529	−2.643 941
1.6	−2.489 362	−2.401 817	−2.418 298
1.7	−2.353 582	−2.305 835	−2.269 037
1.8	−2.224 623	−2.205 414	−2.164 132
1.9	−2.107 282	−2.104 313	−2.078 153
2.0	−2.001 678	−2.005 728	−1.996 563
2.1	−1.906 330	−1.911 981	−1.914 294
2.2	−1.819 653	−1.824 447	−1.831 876
2.3	−1.740 409	−1.743 660	−1.751 781
2.4	−1.667 679	−1.669 533	−1.676 210
2.5	−1.600 736	−1.601 605	−1.606 305
2.6	−1.538 960	−1.539 244	−1.542 228
2.7	−1.481 800	−1.481 795	−1.483 555
2.8	−1.428 766	−1.428 651	−1.429 638
2.9	−1.379 425	−1.379 294	−1.379 829
3.0	−1.333 399	−1.333 290	−1.333 574

cally increases with increasing i. In practice, for angular momentum $l=0$ in Si, the first digit in $Q_{6,6}$ is determined by the eleventh digit in the matrix elements $S_{i,j}$. The magnitude of the diagonal elements $Q_{i,i}$ turns out to be of the order 10^{-i} (for $l=0$ and $l=2$) and the transfer matrix Q is thus rather ill conditioned. For instance, with a 64-bit computation, the seventh significant digit of $Q_{6,6}$ is even influenced by the order of the operations used in calculating terms like $(\alpha_i+\alpha_j)^{n/2}$, which occur in $S_{i,j}$. This inaccuracy propagates further in the computation of the coefficients A_i, as determined from Eq. (2.28) of Ref. 3. It seems of little use to program the explicit expressions, worked out in Ref. 5, since these are quite cumbersome. A more elegant way is to use the fact that the matrix Q is triangular and to rewrite this equation as

$$A_6=-C_6/Q_{6,6}\ ,$$

$$A_i=-\left[C_i+\sum_{l=i+1}^{6} Q_{i,l}A_l\right]\Big/Q_{i,i}$$

$$\text{for } i=5,4,\ldots,1\ .$$

Furthermore, even with sufficient accuracy in the matrix Q, the accuracy of the parameters A_i is clearly directly determined by the rounding of the tabulated values of C_i.

In attempts to reproduce Table V of Ref. 3, we found that the results of the ion-core pseudopotentials for Si depend upon the precision of our various computers. Because of dependency on trivial details of the calculation we find for the coefficients A_i an accuracy of approximately 4 significant digits with 64-bit arithmetic, 9 significant digits with 96-bit arithmetic and 15 significant digits with 128-bit arithmetic. However our $\Delta V_l^{\text{ion}}(r)$ agree to within 10^{-5} hartree (if at least double precision on a 32 -bit computer is used). These last results however differ slightly from Table V of Ref. 3. This is demonstrated in Table I where the BHS results of $\Delta V_l^{\text{ion}}(r)$ are compared with our results obtained on various computers. This leads us to speculate that the potential presented in Table V of Ref. 3 has been calculated with slightly different values for C_i than those presented in Table IV of Ref. 3.

Therefore, for convenience to future users, we give in Table II of this paper the results of the $l=0,1,2$ pseudo-

potential $\Delta V_l^{\text{ion}}(r)$ for Si as we have derived it from the C_i coefficient given in Table IV of Ref. 3. We thus hope that future users of the BHS pseudopotentials will not have to spend time debugging their procedures when in fact they may well be correct despite slight deviations from Table V of Ref. 3.

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[1]D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

[2]M. T. Yin and M. L. Cohen, Phys. Rev. B **25**, 7403 (1982).

[3]G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[4]P. J. H. Denteneer and W. van Haeringen, J. Phys. C **18**, 4127 (1985).

[5]P. C. Pattnaik, G. Fletcher, and J. L. Fry, Phys. Rev. B **28**, 3564 (1983).