1700 PUI K. LAM, MARVIN L. COHEN, AND ALEX ZUNGER

2.0

Structure

Mg (k

22 ANAL YTIC REPRESENTATION FOR FIRST-PRINCIPLES...

0.04

0.02— V r(r) —V~(r) = (Z-,lr)exp(-C, r)

+ phage r(r) +

gsmall r(r) (26)
0

Q

P —0.02
0
—0.04

& —0.0~

—0.08 '-

010 {]] I]]
0 0.5 1.0 1,5 2.0 2.5 3.0 3.5
R {a.u.)
FIG. 4. 4 large r(r) is a good fit for Vz& (x) at large Zn is used as an example.

at -. 1-3 a.u. It turns out that the form

for Z, =18. For completeness, the Ga to Br po-tentials with 3d in the valence and potentials for the 4d with 3d in the core are given in the Appen-dix.

In the work of Andreoni and co-workers, '

the

following expression for V,', was assumed:

V,',(r) = [(6I.)/2r'] exp(-yr), (26)

where both 5I and y are l dependent. For valence states with no core state of the same symmetry, e.g.,

the p state of

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4

2

0
0 0

0 —2

4

12

6— U
0
0

L-

3

0

\

\

\
\
\
\

l Fit

Sb (~=a)

I I I

—10
0 0.5 1.0

R(

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TABLE IV. Fitting parameters for the Z~ =28 potentials. All energies are in Hartree units.

Z =28 C3

V~-Vy
C4

Ug {l =0)
C0 C',

U, (l =1)
C) C2

@Ga
32Ge
33As
- "Se
35Br

3.3476
3.5107
3.6166
3.8322
4.0707

16.367
11.987
9.9995
9.9776
10.190

0.91154
0.964 94
1.345 2
1.4135
1.3565

14.934
14.888
14.954
15.171
15.224

1.8452
1.8923
1.9544
2.0278
2.0910

13.115
12.772
12.779
12.764
12.783

1.8120
1.8373
1.8978
1.9577
2.0218

TABLE V. Tests for the quality of the fitted poten-tials—reproduction of atomic-term values. Energies are given in eV. AE, fit, &, and % denote,

atomill-electron ET BT /Xi6 8.12 Tf 237.146396.98 Tf 27itted

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TABLE VII. Test for the stability of the Ge fitted
potential. Energies are given in eV.

e04~24P

AE
fit

Ge'4s'4p'

AE
fit

- 10.521
- 10.429
+0.092
0.9%

~4s

- 11.430
- 11.339
+0.091
0.8%

-30121

-3.148
+0.027
0.9%

-3.747
-3.780
-0.033
0.9%

Ge+'4s'4p'

AE
fit

4s

- 18.490
- 18.569
-0.079
0.4%

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I I I I

'

I I I I I I I I I I I I I Ne

3.0—

I I I I I I I I I I I I I I I I

10—
Ce

Cp

2.5—

2.0—

Zc = 10

1.0—

Zc =2
e=a

o 4=1 0.5—

I I I I I

2 10

I I I I I I I I I I I I

18 28 36
Z

p I I I I I I I I I I I I I I I I I I 2 10 18 28 36
z

I I I I I I I I III I I I I I I
(c)

I I I I I I I I I I I I I I I I I I

18—

C3

12—

10—

8—

p I I I I I I
2 10

I I I I I I I I I I I I

18 28 36
Z

p
2 10 18
Z

28 36

I I I I I I I I I I I I I I I I I I

(e) I I I I I I I I I I I I I I

40— Zn

C5

35—

c,
30—

C,

10—

Zn

p I
2 10 18
Z

Zc —28

~a.
a

I I I

36

K

20'

0(I I I I I I I (
18 28
Z

4—

K
2—

0 I I I I I I I
18 28

FIG. 8. (a)-(g) Plots of the fitting parameters versus Z, the atomic number.

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duction in the number of indispensable degrees of freedom is achieved relative to conventional

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TABLE IX. Ga to Br potentials with 3d electrons in the core.

Zc =28 C3 C4

Vr-Vv

C~

U) (l =0) c' c'

2

Us (L=1)
C1 C

U) (I=2)
C2
1

C2
2

"Ga

32Ge
33As
'4se

3)Br

3.1536
3.4957
3.6439
3.8456
4.0771

20.4200
10.5530
8.3575
8.0709
8.2950

0.4616
0.8724
1.0930
1.2267
1.2234

57.429
37.634
47.064
51.253
56.430

5.0386
9.8418
11.7040
13.0870
15.0120

14.383
14.846
14.806
15.062
15.161

1.7930
1.8855
1.9387
2.0150
2.0823

12.503
- 12.684
12.598
12.624
12.689

1.7437
1.8228
1.8744
1.9378
2.0060

5.8303
6.0842
6.2339
6.3824
6.5580

1.2501
1.3679
1.4605
1.5552
1.6541

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APPENDIX

The definition of ~oye and valence is rather arbitrary. It is governed only by our chemical in-tuition and the particular applications. For Ga to Br, we treated the 3d electrons as part of the core, but they can also be treated as part of the valence in some applications. Hence, we have also gen-erated the potentials for these elements with the 3d electrons in the valence. The fitting parameters are given in Table VIII. With this definition of the valence, the fitting parameters follow the regular-

ities of the K to Zn row. We have also generated potentials for the 4d electrons with the 3d treated as part of the core. Since the 4d orbital is very