LCAO WAVE-FUNCTIONS AND ENERGIES FOR CUBIC CRYSTALS. III. CONVERGENCE OF SOLUTIONS FOR DIFFERENT LATTICE PARAMETERS

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The LCAO solutions of the total symmetry representation of the cubic point group have been calculated for different values of the lattice parameter. The accuracy of the solutions has been investigated in terms of the total electron charge given by the solutions. Two types of cubic lattices, that of sc and fsc, with an s orbital on each atom have been examined.

1. Lattice parameter and density of states

The LCAO solutions of preceeding papers [1, 2, 3] have been calculated with the lattice parameter a assumed equal to 1 (see Eqs (1) and (22) in [1], Eqs (1) and (5) in [2], Section 4 and Section 6 in [3]). In the Bloch theory the volume v_B of the Brillouin zone is related to that of the atomic cell, v_a, by the equation [4]

$$v_B v_a = 8\pi^3 \tag{1}$$

where

$$v_a \sim a^3. \tag{2}$$

According to Eqs (1) and (2), any vector $\boldsymbol{k}$ changes with a proportionally to $1/a$. Because the parameter a enters the Bloch expression for the LCAO energy E^B as a multiplier of the components of $\boldsymbol{k}$, there is no change in the dependence of E^B on $\boldsymbol{k}$ with a change of a provided that no effect of the interaction integrals on the energy as a function of $\boldsymbol{k}$ is considered. In consequence, the density of states as a function of E^B does not change with a.

A similar situation is observed in the present scheme, though the influence of a on the density of states is less evident. First we introduce a into the Wannier-Slater operator, then solve the corresponding eigenequation in the irreducible representation Γ_1 of the cubic

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TABLE I

The solutions of the WS equation for $a = 2$; sc lattice, 5 sub-band model

λ	m	α_2	$c_{4,m}$	$c_{6,m}$	$c_{8,m}$	$c_{10,m}$
	0	5.186937×10^{-3}	-7.433362	-7.747804×10^{1}	4.326579×10^{1}	1.535017×10^{3}
	1	-4.498335×10^{-3}	1.233420×10^{-5}	-5.372701×10^{-2}	-1.013680×10^{-1}	-6.418676
	2	1.375880×10^{-4}	-1.935856×10^{-4}	1.422906×10^{-2}	5.074128×10^{-3}	1.604795
	3	-2.171482×10^{-6}	2.291643×10^{-4}	-3.340583×10^{-3}	4.923125×10^{-3}	-2.852739×10^{-1}
	4	-3.930282×10^{-7}	-1.511290×10^{-4}	6.321363×10^{-4}	-2.367799×10^{-3}	6.179040×10^{-2}
1	5	2.565940×10^{-7}	7.674619×10^{-5}	-7.029973×10^{-5}	8.480296×10^{-4}	-1.766682×10^{-2}
	6	-1.273390×10^{-7}	-3.442544×10^{-5}	-1.508320×10^{-5}	-2.888010×10^{-4}	6.051367×10^{-3}
	7	5.672453×10^{-8}	1.448827×10^{-5}	1.577273×10^{-5}	9.953903×10^{-5}	-2.250690×10^{-3}
	8	-2.381858×10^{-8}	-5.890502×10^{-6}	-8.412096×10^{-6}	-3.531122×10^{-5}	8.631221×10^{-4}
	9	9.675799×10^{-9}	2.349276×10^{-6}	3.790912×10^{-6}	1.288867×10^{-5}	-3.343832×10^{-4}
	0	6.978583×10^{-3}	-3.200597	3.849273×10^{1}	2.734583×10^{1}	-1.123064×10^{3}
	1	-8.283812×10^{-3}	-3.600508×10^{-6}	1.640588×10^{-1}	3.326526×10^{-1}	8.640822
	2	3.474805×10^{-4}	8.346880×10^{-5}	-2.109761×10^{-2}	-2.487979×10^{-2}	-1.319971
	3	-9.810923×10^{-6}	-8.823153×10^{-5}	2.309752×10^{-3}	-1.211558×10^{-3}	1.270306×10^{-1}
	4	3.693998×10^{-7}	3.839932×10^{-5}	-3.744612×10^{-4}	6.663234×10^{-4}	-1.259548×10^{-2}
2	5	-7.402702×10^{-8}	-1.242357×10^{-5}	8.495935×10^{-5}	-1.679270×10^{-4}	1.359796×10^{-3}
	6	2.298561×10^{-8}	3.574780×10^{-6}	-2.168465×10^{-5}	3.912371×10^{-5}	-1.359951×10^{-4}
	7	-6.673338×10^{-9}	-9.747010×10^{-7}	5.645569×10^{-6}	-9.212984×10^{-6}	7.374327×10^{-6}
	8	1.834231×10^{-9}	2.584815×10^{-7}	-1.465816×10^{-6}	2.223886×10^{-6}	1.935153×10^{-6}
	9	$-4.888637 \times 10^{-10}$	-6.750022×10^{-8}	3.786318×10^{-7}	-5.480583×10^{-7}	-1.050779×10^{-6}

	0	7.664925×10^{-3}	-1.579114	-2.648508×10^{2}	-6.508970×10^{2}	-1.248889×10^{4}
	1	-1.401197×10^{-2}	-7.783063×10^{-6}	-9.482769	-1.944945×10^{1}	-3.424914×10^{2}
	2	7.250080×10^{-4}	3.291137×10^{-4}	2.676896×10^{-1}	5.115847×10^{-1}	1.025018×10^{1}
	3	-1.593019×10^{-5}	4.609241×10^{-5}	2.753426×10^{-2}	6.250173×10^{-2}	9.005360×10^{-1}
	4	2.085408×10^{-7}	-2.594407×10^{-5}	1.849421×10^{-4}	-7.286033×10^{-4}	1.756573×10^{-3}
3	5	2.390236×10^{-8}	6.308071×10^{-6}	-3.071287×10^{-5}	1.268687×10^{-4}	2.810638×10^{-4}
	6	-1.099948×10^{-8}	-1.267339×10^{-6}	-1.799412×10^{-5}	-7.241311×10^{-5}	-0.437082×10^{-4}
	7	2.251109×10^{-9}	2.471880×10^{-7}	2.545787×10^{-6}	1.199921×10^{-5}	1.577128×10^{-4}
	8	$-4.373905 \times 10^{-10}$	-4.769173×10^{-8}	-4.641159×10^{-7}	-2.229048×10^{-6}	-2.955860×10^{-5}
	9	8.525219×10^{-11}	9.112569×10^{-9}	9.615217×10^{-8}	4.398697×10^{-7}	5.924779×10^{-6}
	0	9.854177×10^{-3}	3.592993	1.541906×10^{1}	-1.050127×10^{2}	1.462872×10^{3}
	1	-1.693301×10^{-2}	1.291564×10^{-6}	5.469500×10^{-2}	1.140824×10^{-1}	1.430918×10^{-2}
	2	9.971496×10^{-4}	-5.501293×10^{-5}	-1.234956×10^{-3}	-2.189879×10^{-2}	2.780726×10^{-1}
	3	-3.663302×10^{-5}	4.711179×10^{-5}	-5.646325×10^{-4}	2.132093×10^{-3}	-2.788220×10^{-2}
	4	8.450163×10^{-7}	-9.046167×10^{-6}	7.471243×10^{-5}	-2.435763×10^{-4}	2.458283×10^{-3}
4	5	2.287188×10^{-9}	1.140305×10^{-6}	-8.313780×10^{-6}	3.533093×10^{-5}	-3.450586×10^{-4}
	6	-2.707065×10^{-9}	-1.441912×10^{-7}	1.113338×10^{-6}	-4.858480×10^{-6}	4.861026×10^{-5}
	7	3.893300×10^{-10}	1.951345×10^{-8}	-1.527000×10^{-7}	6.419871×10^{-7}	-6.461194×10^{-6}
	8	$-5.201264 \times 10^{-11}$	-2.639679×10^{-9}	2.048823×10^{-8}	-8.572958×10^{-8}	8.624840×10^{-7}
	9	6.988487×10^{-12}	3.542038×10^{-10}	-2.747719×10^{-9}	1.154916×10^{-8}	-1.160935×10^{-7}
	0	1.294823×10^{-2}	1.090269×10^{1}	-4.208868×10^{1}	1.288361×10^{2}	-8.879524×10^{2}
	1	-2.664131×10^{-2}	-3.302291×10^{-7}	-1.441352×10^{-2}	-3.023014×10^{-2}	4.021535×10^{-1}
	2	1.836487×10^{-3}	2.343566×10^{-5}	-3.825870×10^{-4}	1.251521×10^{-2}	-1.727563×10^{-1}
	3	-7.881186×10^{-5}	-2.004170×10^{-5}	2.209278×10^{-4}	-7.362971×10^{-4}	7.819051×10^{-3}
	4	2.337111×10^{-6}	8.056957×10^{-7}	-3.221207×10^{-6}	-1.652652×10^{-5}	2.979587×10^{-4}
5	5	-5.273177×10^{-8}	1.136473×10^{-7}	-1.030077×10^{-6}	2.866314×10^{-6}	-2.710056×10^{-5}
	6	8.536106×10^{-10}	-4.116512×10^{-9}	1.529840×10^{-8}	4.337911×10^{-10}	-3.428605×10^{-7}
	7	2.567464×10^{-13}	$-5.090765 \times 10^{-10}$	3.918374×10^{-9}	-9.535078×10^{-9}	8.325579×10^{-8}
	8	$-8.530885 \times 10^{-14}$	1.236737×10^{-11}	$-3.720440 \times 10^{-11}$	1.080481×10^{-10}	$-3.500709 \times 10^{-10}$
	9	$-3.630193 \times 10^{-14}$	1.939772×10^{-12}	$-1.294316 \times 10^{-11}$	2.838016×10^{-11}	$-2.333484 \times 10^{-10}$

TABLE II

The almost-free electron density of states $[2\pi^2 v_a^{-1} D(E)]$ for different a; sc lattice, 5 sub-band model

$\varkappa$	$2\pi^2 v_a \varkappa_{(a)}^{-1} D^{c,\lambda}(\varkappa_{(a)})$ from different sub-bands					Total value from columns with $\lambda = 1$ to $\lambda = 5$
	$\lambda = 1$	2	3	4	5	
	$a = 0.5$; Bloch's critical point: $\|k\| = 6.28$					
0.3	4.824327×10^{-2}	1.220591×10^{-1}	2.280199×10^{-3}	8.705160×10^{-2}	4.036587×10^{-2}	3.000000×10^{-1}
0.6	9.648648×10^{-2}	2.441182×10^{-1}	4.560683×10^{-3}	1.741031×10^{-1}	8.073173×10^{-2}	6.000002×10^{-1}
0.9	1.447296×10^{-1}	3.661773×10^{-1}	6.841733×10^{-3}	2.611545×10^{-1}	1.210976×10^{-1}	9.000007×10^{-1}
1.2	1.929724×10^{-1}	4.882365×10^{-1}	9.123624×10^{-3}	3.482056×10^{-1}	1.614634×10^{-1}	1.200002
1.5	2.412151×10^{-1}	6.102958×10^{-1}	1.140662×10^{-2}	4.352564×10^{-1}	2.018291×10^{-1}	1.500003
1.8	2.894574×10^{-1}	7.323553×10^{-1}	1.369099×10^{-2}	5.223069×10^{-1}	2.421949×10^{-1}	1.800005
2.1	3.376993×10^{-1}	8.544149×10^{-1}	1.597696×10^{-2}	6.093570×10^{-1}	2.825605×10^{-1}	2.100009
2.4	3.859409×10^{-1}	9.764748×10^{-1}	1.826476×10^{-2}	6.964067×10^{-1}	3.229262×10^{-1}	2.400013
2.7	4.341820×10^{-1}	1.098535	2.055459×10^{-2}	7.834562×10^{-1}	3.632918×10^{-1}	2.700020
3.0	4.824227×10^{-1}	1.220596	2.284665×10^{-2}	8.705054×10^{-1}	4.036573×10^{-1}	3.000028
3.3	5.306629×10^{-1}	1.342657	2.514108×10^{-2}	9.575544×10^{-1}	4.440229×10^{-1}	3.300038
3.6	5.789027×10^{-1}	1.464719	2.743803×10^{-2}	1.044603	4.843886×10^{-1}	3.600051
3.9	6.271412×10^{-1}	1.586782	2.973761×10^{-2}	1.131652	5.247539×10^{-1}	3.900067
4.2	6.753808×10^{-1}	1.708846	3.203990×10^{-2}	1.218702	5.651195×10^{-1}	4.200088
4.5	7.236193×10^{-1}	1.830911	3.434496×10^{-2}	1.305752	6.054851×10^{-1}	4.500112
4.8	7.718573×10^{-1}	1.952977	3.665280×10^{-2}	1.392802	6.458507×10^{-1}	4.800140
5.1	8.200951×10^{-1}	2.075045	3.896342×10^{-2}	1.479854	6.862165×10^{-1}	5.100174
5.4	8.683327×10^{-1}	2.197115	4.127679×10^{-2}	1.566907	7.265825×10^{-1}	5.400214
5.7	9.165701×10^{-1}	2.319187	4.359285×10^{-2}	1.653961	7.669486×10^{-1}	5.700260
6.0	9.648073×10^{-1}	2.441261	4.591149×10^{-2}	1.741018	8.073149×10^{-1}	6.000313
6.3	1.013045	2.563338	4.823261×10^{-2}	1.828076	8.476815×10^{-1}	6.300373

	$a = 2$; Bloch's critical point: $\lvert k\rvert = 1.57$					
0.3	4.824638×10^{-2}	1.220577×10^{-1}	2.267957×10^{-3}	8.705572×10^{-2}	4.036614×10^{-2}	2.999939×10^{-1}
0.6	9.650995×10^{-2}	2.441045×10^{-1}	4.464656×10^{-3}	1.741325×10^{-1}	8.073340×10^{-2}	5.999450×10^{-1}
0.9	1.448015×10^{-1}	3.661186×10^{-1}	6.528260×10^{-3}	2.612347×10^{-1}	1.211006×10^{-1}	8.997837×10^{-1}
1.2	1.931216×10^{-1}	4.880617×10^{-1}	8.415087×10^{-3}	3.483394×10^{-1}	1.614631×10^{-1}	1.199401
1.5	2.414990×10^{-1}	6.098806×10^{-1}	1.010697×10^{-2}	4.353935×10^{-1}	2.018127×10^{-1}	1.498693
1.8	2.914010×10^{-1}	7.314112×10^{-1}	1.161673×10^{-2}	5.223227×10^{-1}	2.421506×10^{-1}	1.798892
2.1	3.735145×10^{-1}	8.502875×10^{-1}	1.299322×10^{-2}	6.090589×10^{-1}	2.824406×10^{-1}	2.128295
2.4	5.876622×10^{-1}	9.360558×10^{-1}	1.435146×10^{-2}	6.957109×10^{-1}	3.227128×10^{-1}	2.556493
2.7	7.286988×10^{-3}	7.347513×10^{-1}	1.614834×10^{-2}	7.839070×10^{-1}	3.629624×10^{-1}	1.905056
3.0	1.447369×10^{-4}	1.168759×10^{-1}	2.164450×10^{-2}	8.859295×10^{-1}	4.031870×10^{-1}	1.427782

point group, and finally we normalize the solutions A^{Γ_1}. The solutions themselves do not exhibit, in general, a linear dependence on a (see Table I which may be compared with Table II of [1] calculated for $a = 1$), but the quantum parameter $\kappa_{(a)}$ for $a \neq 1$ is related to $\kappa_{(1)}$ exactly by the ratio

$$\kappa_{(a)}/\kappa_{(1)} = 1/a. \tag{3}$$

This is evident from the quantum condition

$$n\pi = \kappa_{(a)} R_{d(a)} \tag{4}$$

which holds for any a and any integer n that is not too small [3]. The term $R_{d(a)}$ is the radius of the crystal sphere with parameter a. Because $R_{d(a)} = aR_{d(1)}$, we obtain Eq. (3).

We now check the constancy of $D(E)$ for different a. This is best done by calculating the density of states for almost-free electrons. In the Bloch case this density is

$$D^B(E) = |k_{(a)}|\,(2\pi^2)^{-1} v_a, \tag{5}$$

whereas in the present scheme [3]

$$D(E) = \sum_{\lambda} \kappa_{(a)}^{-1} [D^{c,\lambda}[\kappa_{(a)}]/v_a] v_a. \tag{6}$$

For a given $\kappa_{(a)}$, the quantity $D^{c,\lambda}[\kappa_{(a)}]/v_a$ is independent of v_a and a (see Eq. (40) in [3]). We now check numerically that (5) is equal to (6) with an accuracy of about six decimal places for $\kappa_{(a)}$ not too large, provided that $|k_{(a)}| = \kappa_{(a)}$. For example, Table II shows $D(E)$ and $D^{c,\lambda}$ for the sc lattice with $a = 0.5$ and $a = 2$. The equality between (5) and (6) has been checked for about 10 values chosen for a and all (sc, bcc and fcc) lattice types in different approximations for the solutions. One may observe that location of the peak of D of (6), corresponding to the critical value of E^B (the touching point of the Brillouin zone), is shifted on the κ-axis roughly also in accordance to Eq. (3).

2. The convergence of solutions

If the A^{Γ_1}-solutions were exact, the shift of the peak with the change of a would be reproduced precisely by (3). The $D(E)$ function — inside the band of the almost-free-electron and the tight-binding approximations — does not depend on the atomic interaction integrals, so it would be the same for any a. The point is that — owing to computational difficulties — we have no accurate solutions for E throughout the band; in the best case, that of the fcc lattice in the tight-binding approximation, good accuracy of $D(E)$ has been attained over 2/3 of the band width [3]. The purpose of the present paper is to investigate how the accuracy of the solutions obtained in a given approximation for A^{Γ_1} depends on a. A measure of accuracy is given by $Q(\mathbf{0})$, the total electron charge at site **0** given by A^{Γ_1} as calculated in the tight-binding approximation for all κ (Eq.(24) in [1] and Eq. (50) in [3]), because, in principle, the densities of all states — also those of large κ — can add up to Q. The results — for sc and fcc lattices — are given in Table III–V; the best solutions are those in which Q is closest to 1. It is evident from the Tables that a relatively good

TABLE III

$Q(\mathbf{0})$ for the sc lattice with different parameter a; four sub-band model; $2m$ is the largest power exponent of $\varkappa$ used in the development of A^{Γ_1} [a]

a \ $m=$	1	2	3	4	5	6	7	8	9
0.5	4.69×10^{5}	1.83×10^{3}	1.42×10^{2}	1.78×10^{2}	7.97×10^{1}	8.23×10^{1}	6.03×10^{1}	5.53×10^{1}	4.91×10^{1}
1	4.23×10^{3}	3.13×10^{2}	7.09×10^{1}	3.66×10^{1}	2.53×10^{1}	2.00×10^{1}	1.69×10^{1}	1.50×10^{1}	1.37×10^{1}
2	2.39×10^{4}	7.90×10^{1}	7.11×10^{1}	2.14×10^{1}	1.53×10^{1}	8.38	1.31×10^{1}	9.12	7.00
4	2.80×10^{4}	8.38×10^{1}	7.54×10^{1}	2.28×10^{1}	1.51×10^{1}	9.06	1.42×10^{1}	9.73	7.35
8	2.91×10^{4}	8.41×10^{1}	7.65×10^{1}	2.36×10^{1}	1.48×10^{1}	9.11	1.35×10^{1}	9.86	7.35

[a] The factor of **2** in the expression $2m$ has been erroneously omitted in the captions of Table II and Table III in [2].

TABLE IV

$Q(\mathbf{0})$ for the sc lattice with different parameter a; five sub-bands model; figure m has the same meaning as in Table III

a \ $m=$	1	2	3	4	5	6	7	8	9
0.5	5.71×10^{5}	9.80×10^{2}	1.43×10^{2}	1.28×10^{2}	8.10×10^{1}	7.11×10^{1}	5.78×10^{1}	5.05×10^{1}	5.24×10^{1}
1	7.40×10^{3}	9.15×10^{1}	2.39×10^{1}	1.47×10^{1}	1.15×10^{1}	1.13×10^{1}	9.67	8.70	8.17
2	2.64×10^{4}	8.47×10^{1}	5.84×10^{1}	2.13×10^{1}	1.30×10^{1}	9.83	1.23×10^{1}	9.63	6.12
4	3.27×10^{4}	8.93×10^{1}	6.06×10^{1}	2.24×10^{1}	1.40×10^{1}	1.11×10^{1}	1.18×10^{1}	9.10	6.62
8	3.37×10^{4}	8.97×10^{1}	6.06×10^{1}	2.24×10^{1}	1.40×10^{1}	1.11×10^{1}	1.18×10^{1}	9.05	6.72

TABLE V

$Q(0)$ for the fcc lattice with different parameter a; four sub-bands model; figure m has the same meaning as in Table III

a \ $m=$	1	2	3	4	5	6
0.5	2.50×10^{4}	4.16×10^{2}	5.84×10^{1}	8.97×10^{1}	4.34×10^{1}	3.81×10^{1}
1	2.18×10^{2}	1.26×10^{1}	5.40	3.71	2.89	2.50
2	1.18×10^{3}	2.53×10^{1}	1.25×10^{1}	1.12×10^{1}	8.10	5.06
4	1.30×10^{3}	2.61×10^{1}	1.36×10^{1}	1.21×10^{1}	8.66	5.04
8	1.31×10^{3}	2.61×10^{1}	1.37×10^{1}	1.22×10^{1}	8.70	5.04

convergence for the sc lattice is attained at about $a = 2$; a further increase of a does not apparently change $Q(\mathbf{0})$ in that case. On the other hand, in the case of the fcc lattice the best solutions are those with $a = 1$; this value of a has been used in all numerical calculations of [3].

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