be a minimum for the correct Φ. The condition for an extremum of $R(\Phi)$ is

$$\begin{aligned}\partial R/\partial\varphi_{\mathbf{h}} = -2\sum_{\mathbf{H}} m(\mathbf{H})\,\Delta E(\mathbf{H})\{&\mathbf{E}_c^*(\mathbf{H})[\partial\mathbf{E}_c(\mathbf{H})/\partial\varphi_{\mathbf{h}}]\\ &+[\partial\mathbf{E}_c^*(\mathbf{H})/\partial\varphi_{\mathbf{h}}]\mathbf{E}_c(\mathbf{H})\}=0 \qquad (4)\end{aligned}$$

for every $\varphi_{\mathbf{h}}\in\Phi$, where $\Delta E(\mathbf{H})$ is $w(\mathbf{H})[E(\mathbf{H})^2-E_c(\mathbf{H})^2]$ for R_1 or $w(\mathbf{H})[E(\mathbf{H})-E_c(\mathbf{H})]/[2E_c(\mathbf{H})]$ for R_2. By working (4) out and assuming a non-centrosymmetric space group, one finds that

$$\begin{aligned}0 &= -4\sum_{\mathbf{H}} m(\mathbf{H})\theta(\mathbf{H})\,\Delta E(\mathbf{H})\\
&\quad\times\sum_s(\partial/\partial\varphi_{\mathbf{h}})\{\mathbf{E}_c(-\mathbf{H})\mathbf{E}(\mathbf{h}R_s)\mathbf{E}(\mathbf{H}-\mathbf{h}R_s)\\
&\quad+\mathbf{E}_c(-\mathbf{H})\mathbf{E}(-\mathbf{h}R_s)\mathbf{E}(\mathbf{H}+\mathbf{h}R_s)\\
&\quad+\mathbf{E}_c(\mathbf{H})\mathbf{E}(\mathbf{h}R_s)\mathbf{E}(-\mathbf{H}-\mathbf{h}R_s)\\
&\quad+\mathbf{E}_c(\mathbf{H})\mathbf{E}(-\mathbf{h}R_s)\mathbf{E}(-\mathbf{H}+\mathbf{h}R_s)\} \qquad (5)\\
&= -4\sum_{\mathbf{H}} m(\mathbf{H})\theta(\mathbf{H})\,\Delta E(\mathbf{H})\\
&\quad\times\sum_s(\partial/\partial\varphi_{\mathbf{h}})\{\mathbf{E}_c(-\mathbf{H}R_s^{-1})\mathbf{E}(\mathbf{h})\mathbf{E}(\mathbf{H}R_s^{-1}-\mathbf{h})\\
&\quad+\mathbf{E}_c(-\mathbf{H}R_s^{-1})\mathbf{E}(-\mathbf{h})\mathbf{E}(\mathbf{H}R_s^{-1}+\mathbf{h})\\
&\quad+\mathbf{E}_c(\mathbf{H}R_s^{-1})\mathbf{E}(\mathbf{h})\mathbf{E}(-\mathbf{H}R_s^{-1}-\mathbf{h})\\
&\quad+\mathbf{E}_c(\mathbf{H}R_s^{-1})\mathbf{E}(-\mathbf{h})\mathbf{E}(-\mathbf{H}R_s^{-1}+\mathbf{h})\} \qquad (6)\\
&= -8\sum_{\mathbf{H}'}\theta(\mathbf{H}')\,\Delta E(\mathbf{H}')(\partial/\partial\varphi_{\mathbf{h}})\{|E(-\mathbf{h})E_c(\mathbf{H}')E(\mathbf{h}-\mathbf{H}')|\\
&\quad\times\cos(\varphi_{-\mathbf{h}}+\varphi_{\mathbf{H}'}+\varphi_{\mathbf{h}-\mathbf{H}'})\} \qquad (7)\\
&= -8E(\mathbf{h})\sum_{\mathbf{H}'}\theta(\mathbf{H}')\,\Delta E(\mathbf{H}')|E_c(\mathbf{H}')E(\mathbf{h}-\mathbf{H}')|\\
&\quad\times\{-\sin\varphi_{\mathbf{h}}\cos(\varphi_{\mathbf{H}'}+\varphi_{\mathbf{h}-\mathbf{H}'})\\
&\quad+\cos\varphi_{\mathbf{h}}\sin(\varphi_{\mathbf{H}'}+\varphi_{\mathbf{h}-\mathbf{H}'})\} \qquad (8)\end{aligned}$$

where R_s is the matrix of the sth point-group symmetry operation and the summation over $\mathbf{H}'$ also includes the reflections related by Laue symmetry. By isolating $\varphi_{\mathbf{h}}$ in (8), the following tangent formula results:

$$\varphi_{\mathbf{h}} = \text{phase of}\left\{\sum_{\mathbf{H}'}\theta(\mathbf{H}')\,\Delta E(\mathbf{H}')\mathbf{E}_c(\mathbf{H}')\mathbf{E}(\mathbf{h}-\mathbf{H}')\right\}. \qquad (9)$$

The correctness of (9) was tested on the same one-dimensional model structure described by Sayre (1952) and Rius & Miravitlles (1991) by using F values instead of E's in R_1. The test calculations with these data showed that (9) was indeed able to refine phases, provided that it was only applied for $|\partial R/\partial\varphi_{\mathbf{h}}|$ values greater than a threshold limit value (TLV), *i.e.* for $|\partial R/\partial\varphi_{\mathbf{h}}|<$ TLV, the old value of $\varphi_{\mathbf{h}}$ was assumed to be its new estimate. The best TLV was empirically determined. If it was chosen too small, the phase-refinement process became unstable. On the contrary, if it was too large, the refinement did not converge.

Finally, combination of (9) with the conventional tangent formula of Karle & Hauptman (1956) leads to the improved tangent formula

$$\begin{aligned}\varphi_{\mathbf{h}} = \text{phase of}\Bigg\{&\sum_{\mathbf{h}'}\mathbf{E}(\mathbf{h}')\mathbf{E}(\mathbf{h}-\mathbf{h}')\\ &+c\sum_{\mathbf{H}'}\theta(\mathbf{H}')\,\Delta E(\mathbf{H}')\mathbf{E}_c(\mathbf{H}')\mathbf{E}(\mathbf{h}-\mathbf{H}')\Bigg\}, \qquad (10)\end{aligned}$$

where the $\mathbf{h}'$ summation only involves the strongest E's, and the $\mathbf{H}'$ summation extends over all reflections. The practical application of (10) requires, however, the prior estimation of the scaling factors $\theta(\mathbf{H}')$, the weighting factors $w(\mathbf{H}')$ and the value of c at the different stages of the phase-refinement process. Practical results will be published elsewhere.

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High-accuracy *ab initio* form factors for the hydride anion and isoelectronic species.

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Abstract

Form factors computed from extremely accurate wave functions are tabulated for H^-, He, Li^+ and Be^{2+} together with fits to Gaussian expansions of the standard form.

Nearly exact *ab initio* form factors are available (Thakkar & Smith, 1978) for the hydride ion and other two-electron atoms. These were computed from extremely accurate wave functions (Thakkar & Smith, 1977) which allow for electron correlation by inclusion of many terms with an explicit dependence on the interelectronic distance. Although the form factors listed in the crystallographic tables (Cromer & Waber, 1974) were computed from Hartree–Fock wave functions which neglect electron correlation completely, they have continued to be used in crystallographic studies. Perhaps this is because the electron-correlated form factors (Thakkar & Smith, 1978) were given in the form of Chebyshev expansions and not in tabular form.

Therefore, we present in Table 1 a listing of these highly accurate form factors for H^-, He, Li^+ and Be^{2+} in the same format as in the crystallographic tables. The correlated form

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Table 1. *Nearly exact form factors for* H^-, He, Li^+ *and* Be^{2+}

The $\lambda^{-1}(\sin\theta)$ values are in Å^{-1}.

Element	H^-	He	Li^+	Be^{2+}
Z	1	2	3	4
$(\sin\theta)/\lambda$	f	f	f	f
0·00	2·0000	2·0000	2·0000	2·0000
0·01	1·9826	1·9982	1·9993	1·9997
0·02	1·9329	1·9930	1·9974	1·9986
0·03	1·8571	1·9843	1·9941	1·9969
0·04	1·7630	1·9722	1·9895	1·9945
0·05	1·6585	1·9568	1·9837	1·9915
0·06	1·5500	1·9383	1·9765	1·9877
0·07	1·4420	1·9168	1·9682	1·9833
0·08	1·3375	1·8925	1·9586	1·9783
0·09	1·2382	1·8655	1·9478	1·9726
0·10	1·1451	1·8362	1·9359	1·9662
0·11	1·0584	1·8046	1·9229	1·9593
0·12	0·9780	1·7711	1·9087	1·9517
0·13	0·9038	1·7358	1·8936	1·9435
0·14	0·8355	1·6990	1·8774	1·9347
0·15	0·7725	1·6608	1·8603	1·9253
0·16	0·7146	1·6216	1·8422	1·9153
0·17	0·6612	1·5816	1·8234	1·9048
0·18	0·6122	1·5408	1·8037	1·8938
0·19	0·5671	1·4996	1·7832	1·8822
0·20	0·5255	1·4581	1·7620	1·8702
0·22	0·4520	1·3750	1·7178	1·8446
0·24	0·3896	1·2926	1·6713	1·8172
0·25	0·3620	1·2519	1·6474	1·8028
0·26	0·3365	1·2118	1·6231	1·7881
0·28	0·2913	1·1336	1·5734	1·7575
0·30	0·2528	1·0584	1·5226	1·7256
0·32	0·2198	0·9866	1·4712	1·6924
0·34	0·1916	0·9186	1·4194	1·6582
0·35	0·1791	0·8860	1·3935	1·6407
0·36	0·1675	0·8545	1·3676	1·6231
0·38	0·1467	0·7942	1·3161	1·5872
0·40	0·1288	0·7378	1·2649	1·5507
0·42	0·1134	0·6852	1·2145	1·5137
0·44	0·1001	0·6362	1·1650	1·4764
0·45	0·0941	0·6131	1·1406	1·4576
0·46	0·0886	0·5907	1·1165	1·4388
0·48	0·0785	0·5486	1·0691	1·4012
0·50	0·0698	0·5095	1·0231	1·3636
0·55	0·0526	0·4241	0·9140	1·2702
0·60	0·0401	0·3541	0·8143	1·1789
0·65	0·0311	0·2966	0·7240	1·0907
0·70	0·0243	0·2494	0·6429	1·0066
0·80	0·0155	0·1785	0·5066	0·8521
0·90	0·0102	0·1300	0·3998	0·7174
1·00	0·0070	0·0962	0·3169	0·6024
1·10	0·0049	0·0723	0·2526	0·5054
1·20	0·0036	0·0552	0·2026	0·4243
1·30	0·0026	0·0426	0·1637	0·3568
1·40	0·0020	0·0334	0·1332	0·3009
1·50	0·0015	0·0265	0·1091	0·2545
1·60	0·0012	0·0212	0·0900	0·2160
1·70	0·0009	0·0172	0·0747	0·1840
1·80	0·0008	0·0140	0·0624	0·1573
1·90	0·0006	0·0116	0·0525	0·1350
2·00	0·0005	0·0096	0·0444	0·1163
2·50	0·0002	0·0042	0·0208	0·0584
3·00	0·0001	0·0021	0·0108	0·0318
3·50	0·0001	0·0012	0·0061	0·0186
4·00	0·0000	0·0007	0·0037	0·0115
5·00	0·0000	0·0003	0·0016	0·0050
6·00	0·0000	0·0001	0·0008	0·0025

factor for H^- deviates from its Hartree–Fock counterpart (Cromer & Waber, 1974) by as much as 0·059 at $\lambda^{-1}(\sin\theta) =$ 0·07 Å^{-1} and the mean deviation between the two is 0·016. Electron correlation affects the form factors of He, Li^+ and Be^{2+} to a much lesser degree; the mean differences between

Table 2. *Parameters for the fits of the nearly exact form factors of Table* 1 *to Gaussian expansions as in equation* (1) *with* $c = 0$

Note that these parameters have been rounded to the least number of significant figures consistent with the stated accuracy of the fits.

	H^-	He	Li^+	Be^{2+}
a_1	0·792	0·9778	1·0025	1·0108
b_1	67·5	7·91	2·97	1·55
a_2	0·677	0·5517	0·53269	0·52818
b_2	17·3	2·50	0·968	0·511
a_3	0·377	0·3816	0·38736	0·38880
b_3	271	21·8	7·84	4·02
a_4	0·152	0·08853	0·077219	0·072042
b_4	3·65	0·563	0·213	0·112

Table 3. *Error measures for the fits using the rounded parameters of Table* 2

	Maximum error	$(\sin\theta)/\lambda$ (Å^{-1})	Mean error
H^-	0·0031	1·1	0·0011
He	0·0016	2·5	0·0004
Li^+	0·0012	5·0	0·0003
Be^{2+}	0·0012	6·0	0·0002

the correlated and Hartree–Fock form factors are 0·001, 0·0005 and 0·0004, respectively, for He, Li^+ and Be^{2+}. It should be noted that the Hartree–Fock wave function does not yield a bound hydride anion while an electron-correlated wave function does.

As a convenience to potential users of our form factors, we have fitted them to Gaussian expansions of precisely the type used in the standard tables (Cromer & Waber, 1974) and in many crystallographic computer programs. This form is given by

$$f(x) = a_1 \exp(-b_1 x^2) + \ldots + a_4 \exp(-b_4 x^2) + c \quad (1)$$

in which $x = \lambda^{-1}(\sin\theta)$. The parameter c has been set to zero since a constant term in the form factor corresponds to an unphysical Dirac delta function in the charge density. Table 2 lists the relevant parameters; these have been rounded to the least number of significant figures possible without sacrifice of the accuracy of the fits. The quality of the fits can be assessed with the help of Table 3 which lists the mean error, the maximum error and the value of $\lambda^{-1}(\sin\theta)$ at which it occurs. These measures, which were computed using the set of rounded parameter, show that our fits are of the same quality as those listed in the standard tables (Cromer & Waber, 1974) for Hartree–Fock form factors of these same systems.

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