neighbour distances in terms of the angle subtended at the centre of the sphere for the hard and soft cases. The hard data are a compilation from Clare & Kepert (1986), Kottwitz (1991), Lazic, Senk & Seskar (1987), Mackay, Finney & Gotoh (1977), Szekely (1974) and Tarnai & Gaspar (1983, 1991).

The case of $N = 24$ for $m = 1$ produces a distorted snub cube which has three near-neighbour distances. As m is increased the three separate values converge to a single value approaching 0.74420 for the true snub cube. Table 4 shows the convergence of the distances with increasing power of m.

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SHORT COMMUNICATIONS

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Improvement of the tangent formula by constraints based on additional information. II. By JORDI RIUS

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Abstract

Recently, Rius & Miravitlles [*Acta Cryst.* (1991). A47, 567–571] have shown the viability of simultaneously refining the phases of the largest structure factors by least-squares minimization of the quantity $R = \sum_H w(H)[F(H)^2 - F_{calc}(H)^2]^2$ where the **H** summation extends over all measured reflections and $w(H)$ is a weighting factor. Here, an alternative method of minimizing R by sequentially refining the phases φ_h of the largest structure factors is suggested that takes advantage of the possibility of expressing $\partial R/\partial \varphi_h = 0$ as an explicit function of φ_h.

Let the residual R be defined according to the expression

$$R_1(\Phi) = \sum_H w(H)m(H)[E(H)^2 - E_c^*(H)E_c(H)]^2, \quad (1)$$

or, alternatively,

$$R_2(\Phi) = \sum_H w(H)m(H)[E(H) - E_c(H)]^2, \quad (2)$$

where Φ represents the collectivity of phases φ_h of the strong normalized structure factors $E(H)$ and **H** denotes the measured reflections in one asymmetrical unit of the reciprocal space. The factor $m(H)$ is the multiplicity of **H** and $w(H)$ is the inverse of the variance associated with the difference $E(H)^2 - E_c(H)^2$ [or $E(H) - E_c(H)$]. Applying Sayre's equation (Sayre, 1952), $E_c(H)$ may be approximated by

$$E_c(H) = E_c(H) \exp i\varphi_H = \theta(H) \sum_{h'} E(h')E(H - h') \quad (3)$$

with $E(h')$ and $E(H - h')$ belonging to the set of strong E's and $\theta(H)$ a scaling factor. Obviously, the residual R will

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

$$\partial R/\partial \varphi_h = -2 \sum_H m(H) \Delta E(H)\{E_c^*(H)[\partial E_c(H)/\partial \varphi_h]$$

$$+[\partial E_c^*(H)/\partial \varphi_h]E_c(H)\} = 0 \qquad (4)$$

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

$$0 = -4 \sum_H m(H)\theta(H) \Delta E(H)$$

$$\times \sum_s (\partial/\partial \varphi_h)\{E_c(-H)E(hR_s)E(H-hR_s)$$

$$+E_c(-H)E(-hR_s)E(H+hR_s)$$

$$+E_c(H)E(hR_s)E(-H-hR_s)$$

$$+E_c(H)E(-hR_s)E(-H+hR_s)\} \qquad (5)$$

$$= -4 \sum_H m(H)\theta(H) \Delta E(H)$$

$$\times \sum_s (\partial/\partial \varphi_h)\{E_c(-HR_s^{-1})E(h)E(HR_s^{-1}-h)$$

$$+E_c(-HR_s^{-1})E(-h)E(HR_s^{-1}+h)$$

$$+E_c(HR_s^{-1})E(h)E(-HR_s^{-1}-h)$$

$$+E_c(HR_s^{-1})E(-h)E(-HR_s^{-1}+h)\} \qquad (6)$$

$$= -8 \sum_{H'} \theta(H') \Delta E(H')(\partial/\partial \varphi_h)\{|E(-h)E_c(H')E(h-H')|$$

$$\times \cos(\varphi_{-h}+\varphi_{H'}+\varphi_{h-H'})\} \qquad (7)$$

$$= -8E(h) \sum_{H'} \theta(H') \Delta E(H')|E_c(H')E(h-H')|$$

$$\times \{-\sin \varphi_h \cos(\varphi_{H'}+\varphi_{h-H'})$$

$$+\cos \varphi_h \sin(\varphi_{H'}+\varphi_{h-H'})\} \qquad (8)$$

where R_s is the matrix of the sth point-group symmetry operation and the summation over H' also includes the reflections related by Laue symmetry. By isolating φ_h in

(8), the following tangent formula results:

$$\varphi_h = \text{phase of}\left\{\sum_{H'} \theta(H') \Delta E(H')E_c(H')E(h-H')\right\}. \qquad (9)$$

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 $|\partial R/\partial \varphi_h|$ values greater than a threshold limit value (TLV), i.e. for $|\partial R/\partial \varphi_h| < \text{TLV}$, the old value of φ_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

$$\varphi_h = \text{phase of}\left\{\sum_{h'} E(h')E(h-h')\right.$$

$$\left.+c \sum_{H'} \theta(H') \Delta E(H')E_c(H')E(h-H')\right\}, \qquad (10)$$

where the h' summation only involves the strongest E's, and the H' summation extends over all reflections. The practical application of (10) requires, however, the prior estimation of the scaling factors $\theta(H')$, the weighting factors $w(H')$ 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