The maximum of E is obtained if all σ_k are -1. The minimum of E is obtained if all σ_k are $+1$, which agrees with the result of Kabsch (1976).

It has also been shown in Kabsch (1976) that $\mathbf{S}+\mathbf{L}$ must be positive definite at the minimum of E. Hence, from (2) the determinants of the two matrices, $\mathbf{U}$ and $\mathbf{R}$, must have the same signs.

In the case that $\det(\mathbf{R}) > 0$, the orthogonal matrix $\mathbf{U}$ corresponding to the minimum of E will be a proper rotation. In the case that $\det(\mathbf{R}) < 0$, an improper rotation will be obtained at the minimum of E (Nyburg & Yuen, 1977). From (9), the smallest residual E corresponding to a best true rotation is then obtained if $\sigma_1=\sigma_2=+1$ and $\sigma_3=-1$ assuming that μ_3 is the smallest eigenvalue of $\tilde{\mathbf{R}}\mathbf{R}$ (three-dimensional vector space). Note that if the smallest eigenvalue is degenerate a best rotation cannot be determined uniquely in the case $\det(\mathbf{R}) < 0$.

Finally, it might be worth mentioning that this procedure can be generalized to find a best unitary matrix to relate two sets of vectors in the complex finite-dimensional vector space.

Summarizing the above results, the following procedure for obtaining a best proper rotation in a three-dimensional vector space is suggested.

(*a*) Remove any translation between the two given vector sets $\mathbf{x}_n$, $\mathbf{y}_n$ and determine $E_0=\frac{1}{2}\sum_n w_n(\mathbf{x}_n^2+\mathbf{y}_n^2)$ and $\mathbf{R}$.

(*b*) Form $\tilde{\mathbf{R}}\mathbf{R}$, determine eigenvalues μ_k and the mutually orthogonal eigenvectors $\mathbf{a}_k$ and sort so that $\mu_1 \geq \mu_2 \geq \mu_3$. Set $\mathbf{a}_3=\mathbf{a}_1\times\mathbf{a}_2$ to be sure to have a right-handed system.

(*c*) Determine $\mathbf{Ra}_k$ $(k=1, 2, 3)$, normalize the first two vectors to obtain $\mathbf{b}_1$, $\mathbf{b}_2$ and set $\mathbf{b}_3=\mathbf{b}_1\times\mathbf{b}_2$. This will also take care of the case $\mu_2>\mu_3=0$.

(*d*) Form $\mathbf{U}$ according to (7) to obtain the best rotation. Set $\sigma_3=-1$ if $\mathbf{b}_3.(\mathbf{Ra}_3)<0$, otherwise $\sigma_3=+1$. The residual error is then $E=E_0-\sqrt{\mu_1}-\sqrt{\mu_2}-\sigma_3\sqrt{\mu_3}$.

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A test for rigid-body vibrations, based on a generalization of Hirshfeld's 'rigid-bond' postulate.

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A simple test for the validity of the rigid-body model for molecular vibrations in crystals is proposed.

Since bond-stretching vibrations for atoms other than hydrogen and deuterium are normally of much smaller amplitude than other vibrations (bond-bending, torsional, rigid-body translational and rotational oscillations), the mean-square vibrational amplitudes of a pair of bonded atoms should be equal along the bond direction, even though they may be widely different in other directions. As Hirshfeld (1976) has pointed out, this provides a necessary (although by no means sufficient) condition that thermal ellipsoids derived by X-ray analysis represent genuine vibrational ellipsoids. If the condition is seriously violated, the U_{ij} values may be suspected of being contaminated by charge-density deformation contributions or absorption or other systematic errors.

Hirshfeld's 'rigid-bond' postulate can be expressed in a more general (though somewhat weaker) form as a 'rigid-body' postulate and used as a simple test for the validity of the rigid-body model of any molecule for which U_{ij} values are available. Since rigidity implies that *all* distances within a body remain invariant, all pairs of atoms in a rigid molecule can be regarded as being connected by virtual bonds. Hence the equality condition should hold for all such pairs of atoms as well as it does for bonded pairs. Conversely, when the data satisfy the rigid-bond test, gross violation of the equality condition for certain pairs of non-bonded atoms within a molecule should indicate that the rigid-body model is inappropriate for the molecule in question and might also provide some hints about the nature of the internal motions within the molecule.

With these ideas in mind, we have calculated mean-square vibrational amplitudes $z^2_{A,B}$ in the AB direction for all pairs of atoms in several molecules from U_{ij} values obtained by conventional least-squares refinement. We find that the condition $\Delta_{A,B}=z^2_{A,B}-z^2_{B,A}\sim 0$ is obeyed well in cases where least-squares analysis of the vibration tensors in terms of rigid-body $\mathbf{T}$, $\mathbf{L}$ and $\mathbf{S}$ tensors (Schomaker & Trueblood, 1968) leads to good agreement between U_{ij}(obs.) and U_{ij}(calc.) values. This is hardly surprising, since the condition $\Delta_{A,B}=0$ is obeyed *exactly* for the rigid-body model.

More interesting are examples where the rigid-body analysis leads to poor agreement between U_{ij}(obs.) and U_{ij}(calc.). We discuss here one illustrative example in detail, that of 3-phenyl-3-benzyl-*N*-methylsuccinimide (Fig. 1), the crystal structure of which has recently been determined (at 100 K) in our laboratory. The $z^2_{A,B}$ values for the 21.20/2 directions between all pairs of C, N and O atoms are

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Table 1. *Values of* $|\Delta_{A.B}| \times 10^4$ (Å^2) *for all atom pairs* (*bonded pairs are in parentheses*)

See Fig. 1 for atomic numbering.

	O(1)	O(2)	N	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)	C(13)	C(14)	C(15)	C(16)	C(17)	C(18)
O(1)	0	18	7	(50)	8	16	33	17	9	18	7	12	36	86	9	67	19	31	46	36	28
O(2)		0	20	7	1	4	(22)	1	26	117	108	122	115	36	43	9	56	61	19	9	17
N			0	(22)	39	6	(17)	(2)	3	57	22	22	5	51	9	13	72	65	47	31	47
C(1)	Imide			0	(22)	42	3	3	1	11	40	45	87	154	88	34	97	61	36	15	13
C(2)	–imide				0	(21)	17	29	(12)	35	32	17	16	43	43	(31)	64	8	12	9	9
C(3)						0	(11)	10	16	35	35	51	7	48	41	17	61	17	15	28	4
C(4)							0	11	9	40	19	42	42	90	44	13	72	66	17	18	1
C(5)								0	35	124	120	156	149	161	167	12	5	9	6	2	21
C(6)									0	(6)	39	8	26	23	65	0	53	15	7	42	30
C(7)										0	(3)	2	19	1	(15)	15	97	18	20	48	39
C(8)											0	(7)	8	6	14	39	26	47	34	10	7
C(9)				Benzyl					Benzyl			0	(20)	19	4	30	37	37	28	21	11
C(10)				–imide					–benzyl				0	(49)	13	1	76	8	19	66	57
C(11)														0	(3)	78	4	67	63	20	21
C(12)															0	82	23	55	68	48	53
C(13)																0	(2)	15	18	7	(12)
C(14)																	0	(36)	7	9	1
C(15)				Phenyl					Phenyl							Phenyl		0	(0)	13	4
C(16)				–imide					–benzyl							–phenyl			0	(8)	13
C(17)																				0	(8)
C(18)																					0

conveniently arranged as in Table 1. The r.m.s. value of Δ for the 23 bonded pairs of atoms (in parentheses in the table) is 21×10^{-4} Å^2, to be compared with an estimated $\sigma(\Delta) \sim 15 \times 10^{-4}$ Å^2. The r.m.s. Δ's for non-bonded pairs *within* each of the three groupings, *N*-methylsuccinimide (eight atoms), benzyl (seven) and phenyl (six), are 19, 24 and 11 (all $\times 10^{-4}$) Å^2 respectively, no larger than for the bonded pairs. However, the r.m.s. Δ's for non-bonded pairs *between* these three groupings are significantly larger: 71×10^{-4} for imide–benzyl, 38×10^{-4} for imide–phenyl, and 44×10^{-4} Å^2 for benzyl–phenyl. Even casual inspection of Table 1 shows that low Δ values tend to be concentrated in three blocks bordering the main diagonal, with the large Δ values (all those greater than, say, 50×10^{-4} Å^2) in the off-diagonal blocks corresponding to inter-group pairings.

This analysis of the $z^2_{A,B}$ values indicates that non-bonded distances within the individual groups are not significantly less rigid than the bonds themselves, in other words, that the groups behave as more or less rigid bodies, while there are considerable relative motions between them. However, it is not so easy to establish the nature of these motions. One possibility is to postulate the existence of certain specific kinds of motion (*e.g.* torsional oscillations about bonds) and estimate their magnitudes by including appropriate parameters in a modified Schomaker–Trueblood type of analysis (Dunitz & White, 1973).

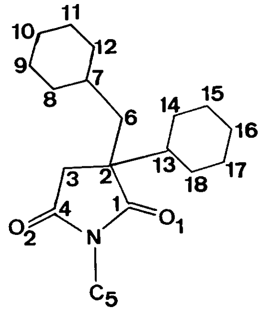

Fig. 1. Atomic numbering for 3-phenyl-3-benzyl-*N*-methylsuccinimide.

Programs *THMB*-2 or *THMI*-2 (Trueblood, 1977, 1978) for analysis of thermal-motion ellipsoids in crystals provide options for the automatic calculation of $z^2_{A,B}$ values and torsional oscillations about bonds.

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