VOLUME 50, NUMBER 21 PHYSICAL REVIEW LETTERS 2) MAY 1985 Simultaneous Relaxation of Nuclear Geometries and Electric Charge Densities

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'

v'+U(r)]y, (r) = c, y, (r),
and its corresponding

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density p, i.e.,

BR„„,„~R„-R„.[' dr'
Unfortunately, this puristic theorem is of little
practical help. It holds only for p calculated
from the exact g (or certain types of fully opti-
mized g) and when p is exactly self-consistent. In practice, the linear combinations over finite basis sets which are used to expand g do not provide exact eigenstates to H = --,

' V'+ U. Fur-
thermore, general points on the 8, -p hypersur-face do not correspond to self-consistent p. This often leads to huge errors in the calculated forces, rendering F

" useless, even if the
basis set produces acceptably small errors' in E. Fortunately, however, one

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v(p,, R) —p, =0,

Fn (pi R) +Fn (pi R) =0i

(9)

then when Eq. (9) (where F„' does not appear)

correct electrostatic result is F~" =0. In real-
ity, a small field-induced distortion of p(r) will cancel exactly the nuclear force eZ E. In the
present formulation, the force F„"of Eq. (7a)
will correct the first-order error of F due to the charge distortion

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(1982).
8In the special case vrhere U is chosen to be linear in
each p, I. e.g., a fixed function f(Fi plus a Fourier series
with coefficients p» cf. Ref. 3j, the stationarity condi-
tion becomes simply Z& {v&—p&) gpss

=0 where pe~ is
the linear response matrix.
~U. Linefelt and A. Zunger, Phys. Rev. B 24, 5913 (1982).

' P. Pulay, Mol. Phys. 17, 197 (1969). "J.Ibm, M. T. Yin, and M. L. Cohen, Solid State

32 687.45 tmmunT /Xi4 9.58 Tf 43029 68749 Td (p,)1

32 687.4549T /Xi4 12.6 Tf 200.32 n

co&