

# The General Form of Pseudopotential Operators

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Received May 15, 1971

The general form of hermitean linear pseudopotential operators, which are independent of the virtual energies, is derived. A special case of this pseudopotential is the usually used one,  $|c\rangle(\varepsilon - \varepsilon_c) < c|$ . It is shown that any pseudopotential is of essentially non-local character. The significance of  $\varepsilon$ -dependency and non-hermiticity of pseudopotentials is discussed. The advantages of semiempirical model hamiltonians in comparison with exact pseudopotential hamiltonians are stressed.

Die allgemeine Form hermitescher linearer Pseudopotentialoperatoren, die die virtuellen Orbitalenergien nicht enthalten, wird angegeben. Eine spezielle Form hiervon ist das üblicherweise verwendete Potential  $|c\rangle(\varepsilon - \varepsilon_c) < c|$ . Es wird gezeigt, daß jegliches Pseudopotential wesentlich nichtlokalen Charakter hat. Die Bedeutung von  $\varepsilon$ -Abhängigkeit und Nicht-Hermitizität von Pseudopotentialen wird diskutiert. Der Vorzug von Modell-Hamiltonoperatoren gegenüber exakten Pseudo-Operatoren wird betont.

Expression générale des opérateurs de pseudo-potential linéaires hermitiques, indépendants des énergies des orbitales virtuelles. Le pseudo-potential ordinairement utilisé  $|c\rangle(\varepsilon - \varepsilon_c) < c|$  en est un cas particulier. On montre que tout pseudo-potential a essentiellement un caractère non local. Discussion de la signification de la dépendance à  $\varepsilon$  et de la non-hermiticité des pseudo-potentiels. On souligne les avantages des hamiltoniens modèles semi-empiriques par rapport aux hamiltoniens de pseudo-potential exact.

## 1. Introduction

Be given a system of Hartree-Fock-equations

$$\begin{aligned} F(c, v)|c\rangle &= \varepsilon_c|c\rangle \\ F(c, v)|v\rangle &= \varepsilon_v|v\rangle \\ F(c, v)|u\rangle &= \varepsilon_u|u\rangle \end{aligned} \quad (1)$$

where  $c$  means low lying core orbitals,  $v$  the higher valence ones, and  $u$  the unoccupied virtual orbitals. They form a complete set  $\{c, v, u\} = \{i\}$ ; in the following  $i, j$  refer to any orbital,  $k, l$  to any non-core orbital.

A pseudopotential operator  $V_{ps}$  is defined [1, 2] as an operator so that the solutions of the equation

$$[F + V_{ps}(\tilde{\varepsilon})|\tilde{\psi}\rangle = \tilde{\varepsilon}|\tilde{\psi}\rangle \quad (2)$$

will satisfy the following two requirements:

1. the eigenvalues  $\tilde{\varepsilon}$  are just the  $\varepsilon_k$  of Eq. (1) and there exist no lower ones,
2. the eigenfunctions (pseudo-orbitals)<sup>1</sup>  $|\tilde{\psi}\rangle = |\tilde{k}\rangle$  have the form

$$|\tilde{k}\rangle = |k\rangle + \sum_c a_{kc}|c\rangle \quad \text{for } \tilde{\varepsilon} = \varepsilon_k \quad (3)$$

<sup>1</sup> The pseudo-orbitals so defined are not normalized to unity.

where the  $a_{kc}$  are suitable constants (i.e. the  $a_{kc}$  are to take such values that the function  $|\tilde{k}\rangle$  will be rather smooth and nodeless in the core-region and may be approximated by rather few basis functions, e.g. of simple Slater type).

Obviously  $V_{ps}$  is not uniquely determined by this. Usually it is stated [1] that it is sufficient to require  $V_{ps}$  to be hermitean in order to get a unique expression for  $V_{ps}$  which is given as

$$V_{ps} = \sum_c |c\rangle (\tilde{\epsilon} - \epsilon_c) \langle c|. \quad (4)$$

In the following chapter it will be shown, that Eq. (4) is only a special form of a hermitean pseudopotential.

## 2. Hermitean Linear Pseudopotentials

We will require  $V_{ps}$  to be not only a hermitean operator, but a linear one, too. This is quite reasonable from the practical point of view. The general form of a linear hermitean operator is given by

$$V_{ps}(\epsilon) = \sum_{i,j} |i\rangle v_{ij}(\epsilon) \langle j|, \quad v_{ij}^* = v_{ji} \quad (5)$$

where the matrix elements  $v_{ij}$  may only depend *parametrically*<sup>2</sup> on  $\epsilon$ , but not explicitly on the  $a_{kc}$ . Substitution of  $V_{ps}$  and  $|\tilde{\psi}\rangle$  in Eq. (2) by Eqs. (3, 5) and using Eq. (1) and the completeness of  $\{i\}$  leads to the following set of linear equations for the pseudopotential coefficients  $v_{ij}$ :

$$\begin{aligned} -v_{ck}(\epsilon_k) &= \sum_{c'} a_{kc'} \cdot v_{cc'}(\epsilon_k) + (\epsilon_c - \epsilon_k) a_{kc} \\ -v_{lk}(\epsilon_k) &= \sum_{c'} a_{kc'} \cdot v_{lc'}(\epsilon_k) \end{aligned} \quad (6)$$

which however let most of the  $v_{ij}$  undetermined.

There are two ways to make the  $v_{ck}(\epsilon)$  independent of  $a_{kc}$ :

1. *The  $a_{kc}$  must be prechosen* as functions of  $\epsilon$ :  $a_{kc} = a_c(\epsilon_k)$ . It requires, to be sure, some crude knowledge on the behavior of the valence and virtual orbitals in the core region; however, this will usually be no bad draw-back. The valence orbitals must be known in any case, for the construction of  $F(c, v)$  (see Chap. 4). And the behavior of all non-core orbitals of the same symmetry  $\gamma$  is very similar in the core region, as is known empirically. This means that it is not crucial to choose some suitable functions  $a_c(\epsilon)$  which, except for different symmetries  $\gamma$ , will vary with  $\epsilon$  even very slowly. Thus we may choose the  $a_{kc}$  (and consequently  $V_{ps}$ , too) as mainly symmetry-dependent only:  $a_{kc} = a_c(\epsilon_k) = a_c(\gamma_k)$ . If it should be possible to construct the  $v_{ij}(\epsilon)$  without any previous knowledge of all the virtual  $\epsilon_i$ , then the  $v_{cl}(\epsilon)$  should be independent of  $l$  (see Eq. (6)) and consequently

<sup>2</sup> Strictly speaking,  $\epsilon$  is not a parameter but the eigenvalue of Eq. (2); that is potential (5) is really non-local. In practise however, as discussed in Chap. 4.5, the  $\epsilon$ -dependency of  $V_{ps}$  is very weak. Thus one commits a negligible error only, by treating  $\epsilon$  in Eq. (5) as a parameter suitably chosen before the beginning of the iterative solution of Eqs. (2, 5).

the  $v_{lk}$ , too. One then obtains

$$\begin{aligned} v_{cc'}(\varepsilon) &= (\varepsilon - \varepsilon_c) \delta_{cc'} + w_{cc'}(\varepsilon) \\ v_{cl}(\varepsilon) &= - \sum_{c'} a_{c'}(\varepsilon) \cdot w_{cc'}(\varepsilon) \\ v_{kl}(\varepsilon) &= \sum_{c'c''} a_{c'}(\varepsilon) \cdot a_{c''}^*(\varepsilon) \cdot w_{c'c''}(\varepsilon) \end{aligned} \quad (7)$$

with arbitrary functions  $w_{cc'}(\varepsilon) = w_{c'c}^*(\varepsilon)$ .

2. The second possibility is to set

$$\begin{aligned} v_{cc}(\varepsilon) &= \varepsilon - \varepsilon_c \\ v_{cc'}(\varepsilon) &= v_{cl}(\varepsilon) \equiv 0 \quad (c \neq c') \\ v_{kl}(\varepsilon) &= \begin{cases} 0 & \text{if } \varepsilon = \varepsilon_k \text{ or } \varepsilon = \varepsilon_l \\ \text{arbitrary value} & \text{otherwise.} \end{cases} \end{aligned} \quad (8)$$

In this case *the  $a_{kc}$  will become undetermined.*

In an actual numerical calculation they will take values according to the numerical approximations used [2]. E.g. in the work of Szasz and McGinn [3], Eq. (2) is solved by numerical integration; accordingly the  $a_{kc}$  will then take values which causes all the higher derivatives of  $|\tilde{w}\rangle$  to vanish approximately. Thus it is understandable that the pseudoorbitals calculated by Szasz and McGinn are definite and rather smooth.

A special case of Eqs. (8) is to set  $v_{kl}(\varepsilon) \equiv 0$ , in which case a previous knowledge of all the  $\varepsilon_i$  is not necessary. Then, one obtains the expression (4) for  $V_{ps}$ , which is the generally used one [1-3]. Another way to obtain Eq. (4) is to choose the  $w_{cc'}(\varepsilon)$  of Eqs. (7) identical to zero.

Accordingly Eqs. (7) represent the most general expression of hermitean linear self-consistent pseudopotentials.

### 3. The Non-Local Character of the General Pseudopotential

In this chapter it shall be proved that it is *impossible to substitute any pseudopotential by a local potential.* This is the case not only for the special form (4) which lets the core mixing coefficients indefinite, but also for every general  $V_{ps}$ , Eqs. (7), which leads to quite well defined pseudoorbitals. A first hint to this fact may be seen in the symmetry-dependence of the  $v_{ij}$ , as mentioned in the preceding chapter.

For simplicity we will confine ourselves to a system with only one core orbital. Then the matrix representation of  $V_{ps}$  in the basis  $\{i\}$  is given by

$$V_{ps} = (\varepsilon - \varepsilon_c) \cdot \begin{pmatrix} 1 & 0 & \dots \\ 0 & 0 & \dots \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix} + w_{cc}(\varepsilon) \cdot \begin{pmatrix} 1 & \alpha(\varepsilon) & \dots \\ \alpha^*(\varepsilon) & |\alpha(\varepsilon)|^2 & \dots \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix} \quad (9)$$

Now let us assume, that some  $V_{ps}$  is equivalent to a local potential  $V(x)$ . For  $V(x)$  we make the general ansatz

$$V(x) = (\varepsilon - \varepsilon_c) \cdot V^1(x) + w_{cc}(\varepsilon) \cdot V_\varepsilon^2(x). \quad (10)$$

As  $V^1(x)$  is only a special form of  $V_\varepsilon^2(x)$  we will restrict our discussion to the latter one. We now expand  $V^2(x)$  in a series of our basis functions  $i(x)$ ,  $v_i$  being the expansion coefficients:

$$V^2(x) = \sum_i v_i \cdot i(x). \quad (11)$$

Using the abbreviation<sup>3</sup>

$$S_{ijk} = \int i(x) \cdot j(x) \cdot k(x) \cdot dx \quad (12)$$

the matrix representation of  $V^2(x)$  reads as

$$V_{ij}^2 = \sum_k S_{ijk} \cdot v_k. \quad (13)$$

If a local pseudopotential really is to exist, the “ $N$ ” values  $v_k$  should be a solution of the  $\frac{“N^2”}{2}$  linear equations

$$\sum_k S_{ijk} \cdot v_k = \alpha^{2 - \delta_{ci} - \delta_{cj}}. \quad (14)$$

We now construct two functions  $g(x) = \sum_i g_i \cdot i(x)$  and  $h(x) = \sum_i h_i \cdot i(x)$  with  $g(x) \cdot h(x) \equiv 0$ , but both  $g(x)$  and  $h(x) \not\equiv 0$ , and for which the integrals used below are to exist. Then

$$I = \int g(x) \cdot h(x) \cdot V(x) \cdot dx = 0. \quad (15)$$

On the other hand, using Eq. (14), one obtains

$$I = \sum_{i,j} g_i \cdot h_j \cdot \int i(x) \cdot j(x) \cdot V(x) \cdot dx = \sum_{i,j} g_i \cdot h_j \cdot \alpha^{2 - \delta_{ci} - \delta_{cj}}. \quad (16)$$

As the functions  $g(x)$ ,  $h(x)$  are not uniquely defined, expression (16) may take any value, except all  $\alpha^v = 0$ , that is  $v_k = 0$  and  $V(x) \equiv 0$ . From this contradiction it follows that no *local* pseudopotential can exist.

#### 4. Concluding Remarks

1. To summarize, it is possible to construct a great many of different pseudopotential operators. This is even the case, if  $V_{ps}$  is to be linear, hermitean and built up without use of the  $\varepsilon_i$ . In this case, the most general form of  $V_{ps}$  is given by Eqs. (5, 7). No special form of it may be replaced by a local potential. This is no contradiction to the empirical fact (see for example Ref. [4]), that for atoms  $V_{ps}$  may very well be approximated by the model potential

$$V_M = \sum_\gamma V^\gamma(x) \cdot P^\gamma \quad (17)$$

<sup>3</sup> In this chapter the index  $k$ , too, refers to any orbital  $c, v, u$ .

where  $P^\gamma$  is an operator which projects on the subspace of symmetry species  $\gamma$ , and where the  $V^\gamma(x)$  are local potentials<sup>4</sup>. The model potential (17) is of *essentially non-local* character, too, and leads to definite values of the  $a_{kc}$ , as is the case with the exact general potential  $V_{ps}$ . It is probable that for systems without high symmetry the approximation (17) will not be a good one. How one has to choose a model potential for molecules has recently been discussed in Ref. [5].

2. Till now it has not been shown that  $V_{ps}$  is a "variational potential" [1] i.e. that Eq. (2) will have no low lying core-like solutions. Indeed, this is not the case for the usually used  $V_{ps}$ , Eq. (4), which fact has recently been stressed [6]. On the other hand it is obvious that one can always choose the  $a_c(\varepsilon)$  in Eqs. (7) or the  $V(x)$  in Eq. (17) so as  $V_{ps}$  or  $V_M$ , resp., to be variational potentials.

3. If the pseudopotential operator (5) is to contain *core orbitals only*, all  $v_{ci}$ ,  $v_{kl}$  of Eq. (7) must be zero. This may be achieved by two ways: a)  $w_{cc} \equiv 0$ , leading to Eq. (4) or b)  $a_c \equiv 0$ , that is the valence orbitals will not be smooth. Thus, under the above requirement, Eq. (4) is the *only* hermitean pseudopotential to yield smooth nodeless pseudoorbitals.

The most general pseudopotential discussed till now is that of Austin [7]

$$V_{ps}^A = \sum_c |c\rangle \langle F_c| \quad (18)$$

with arbitrary functions  $F_c$ . It is a non-hermitean generalisation of (5). It *may* lead to smooth pseudoorbitals; this has been ascribed [18] to the non-hermiticity of (18). If the general expansion of  $F_c$

$$|F_c\rangle = \sum_c f_{c'c} |c\rangle + \sum_k f_{c'k} |k\rangle \quad (19)$$

and (18) are substituted into Eq. (2), one obtains for any  $c'$

$$\sum_c [f_{c'c} + \delta_{c'c}(\varepsilon_c - \varepsilon_k)] a_{kc} = -f_{c'k} \quad (20)$$

Now if  $V_{ps}^A$  and consequently the  $F_c$  contain core orbitals only, i.e.  $f_{c'k} = 0$ , Eqs. (20) generally will have the trivial solution  $a_{kc} = 0$  only – except the special case where  $\text{Det}[f_{c'c} + \delta_{c'c}(\varepsilon_c - \varepsilon_k)] = 0$ ; then the  $a_{kc}$  will not be uniquely determined, as with pseudopotential (4).

Thus we conclude: in order to obtain smooth and definite pseudoorbitals, the pseudopotential has to contain a *non-core projection* portion. This is independent from whether we confine to hermitean potentials or not.

4. Finally a remark is to be made on the practical utility of exact pseudopotentials. To start pseudopotential theory with Eq. (2) is rather disadvantageous, as it requires the previous knowledge of the valence orbitals. On the other hand, to start with  $F(c, \tilde{v})$ , or  $F(c, \mathcal{O}_c \cdot \tilde{v})$  – where  $\mathcal{O}_c$  is an operator which orthonormalizes

<sup>4</sup>  $\gamma$  will usually describe space symmetry. In atoms e.g.  $\gamma$  is the angular momentum quantum number  $l$ . With such effective potentials and using  $\left(\frac{\alpha^2}{2r} \cdot \frac{\partial V}{\partial r}\right) l_s$  as spin orbit coupling operator it is however often principally impossible to reproduce the true spin-orbit splitting. This has shown up in the alkali metal atom spectra (unpublished results) where the spin-orbit splitting seems to be greatly reduced by CI with excited core states. In such cases it might be necessary to introduce atomic model potentials which are  $(j = l + s)$ -dependent.

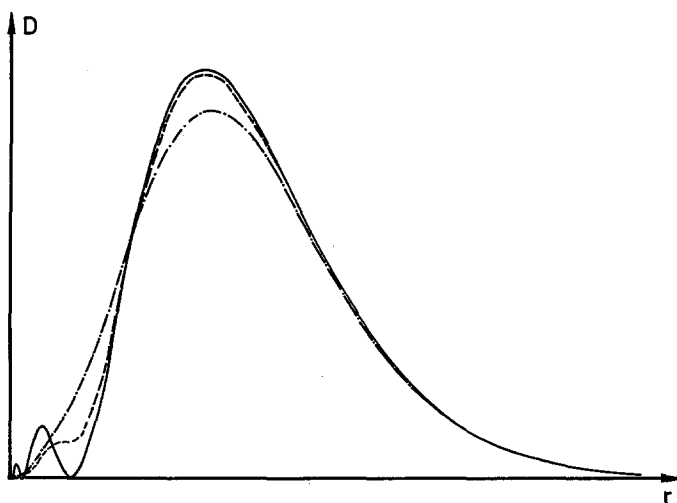


Fig. 1. Radial valence electron density  $D(r)$  of Na 3s orbital ——— SCF-values; - - - - - smoothest pseudo-density of pseudoorbital defined by Eq. (3); - · - · - · - "optimum" pseudo-density corresponding to Eq. (21-22)

on the core space — instead of  $F(c, v)$ , as has been suggested at times [1-3, 5], will always lead to non-linear pseudopotentials if they are defined as above, because two-valence-electron terms will then be contained in them<sup>5</sup>. Such a method, as has been used by Logatchov [9], is unsatisfactorily complicated. Furthermore pseudoorbitals as defined by Eq. (3), or numerical approximations to them as those of Szasz and McGinn [3], are somewhat unfavourable, since the calculation of valence-electron expectation values from the  $|\tilde{k}\rangle$  is rather troublesome. According to our definition pseudodensities are less than the true valence electron densities outside the core region by about  $a^2$  ("normalization error"), and correspondingly do not reproduce the "orthogonalization hole" of the same magnitude in the true valence electron density near the nucleus (see Fig. 1). It would be more favourable to have pseudoorbitals with the following properties: they should be *equal to the true valence and virtual orbitals outside the core region*, and should be *nodeless and rather smooth*<sup>6</sup> *inside* and reproduce the mean valence electron density there, as shown in the figure. With such pseudoorbitals  $|\tilde{k}\rangle$  the approximation  $\langle \tilde{k} | A | \tilde{k} \rangle \approx \langle k | A | k \rangle$  would be a very good one for a great variety of operators  $A$ . However, they will correspond to a rather slowly convergent series in a set of *all* (canonical or natural) orbitals,

$$|\tilde{k}\rangle = |k\rangle + \sum_{i(\neq k)} b_{ki} |i\rangle. \quad (21)$$

Thus it seems impossible to obtain a simple and practical but rigorous pseudo-potential theory.

<sup>5</sup> A linear approximation to it (Eq. (3c) of Ref. [6]) has recently been investigated. Contrary to Eqs. (2, 4) of this work, it will usually be a variational pseudohamiltonian.

<sup>6</sup> I.e., it is not optimum to look for the "smoothest" pseudoorbitals as suggested by some authors [10].

5. From the *practical* point of view it may be optimum, instead of Eq. (2) to use the *semiempirical* one

$$|F(c, \tilde{\psi}) + V_M|\tilde{\psi}\rangle = \tilde{\varepsilon}|\tilde{\psi}\rangle \quad (22)$$

with some experimentally adjusted model potential functions  $V_M^\gamma(x)$  (Kombiniertes Näherungsverfahren of Hellmann [11]), or in order to allow for valence electron correlation to use a corresponding many-valence-electron hamiltonian as recommended in Refs. [1, 5]. As is seen from Eqs. (7), any exact  $V_{ps}$  is explicitly dependent on the orbital energy of that orbital, on which it acts.

Shaw [12] has shown that with pseudo-orbitals and -potentials defined as usual (Eqs. 2, 3),  $\langle \tilde{k} | \frac{\partial V_{ps}}{\partial \varepsilon} | \tilde{k} \rangle$  is a direct measure of the normalization error and orthogonalization hole. Now let us calculate  $\langle \partial V / \partial \varepsilon \rangle$  with the pseudoorbitals  $\tilde{k}$ , Eq. (21), which don't show the normalization error by definition. By differentiation of the Eq.  $|F(c, k) + V_M(\varepsilon_k)|\tilde{k}\rangle = \varepsilon_k|\tilde{k}\rangle$  with respect to  $\varepsilon_k$  and by using  $F = \sum_i |i\rangle \varepsilon_i \langle i|$  one obtains

$$\frac{\partial V}{\partial \varepsilon} |\tilde{k}\rangle = |\tilde{k}\rangle - |k\rangle - (F + V - \varepsilon_k) \left| \frac{\partial \tilde{k}}{\partial \varepsilon} \right\rangle. \quad (23)$$

Multiplying by  $\langle \tilde{k} |$  leads to

$$\langle \tilde{k} | \frac{\partial V}{\partial \varepsilon} | \tilde{k} \rangle = \sum_{i(\neq k)} b_{ki}^2 - \langle \tilde{k} | F + V - \varepsilon_k \left| \frac{\partial \tilde{k}}{\partial \varepsilon} \right\rangle. \quad (24)$$

If we assume the general pseudopotential  $V$  to be hermitean the last term of (24) will vanish, and the lhs. will usually be of the order of  $+10^{-1}$ . Thus it follows that an exact pseudopotential will increase with  $\varepsilon$  in any case, i.e. too with pseudo-orbitals that show no normalization error and correctly reproduce the orthogonalization hole in the mean. Several authors [13, 14] have recommended and used  $\varepsilon$ -dependent model potentials  $V^\gamma(x, \varepsilon)$ . Disadvantages of such potentials, however, are:

1. every calculation will be an iterative process;
2. CI-calculations must be done using canonical orbitals as basis functions; in any other beyond-HF-calculation it is not clear what a value of  $\varepsilon$  to be used;
3. the number of parameters to be adjusted in the model potential is increased.

Nevertheless it should not be concealed that the neglect of an  $\varepsilon$ -dependency in a variety of model potentials indeed leads to small systematical errors. This may be seen e.g. from spectral data of one-valence electron systems (see Table 2 of Ref. [4a]) or electron-atom scattering phase shifts [14]. According to these empirical results the model potential should slightly increase with  $\varepsilon$ , as is theoretically predicted. However it seems possible largely to reduce the errors by explicitly allowing for incomplete screening and core-valence-exchange and -correlation through some local potential (Ref. [15] and unpublished results), i.e. by model potentials which show a much more pronounced valley near the outer core regions than the potentials applied usually.

Furthermore, results of thermo-power calculations on liquid metals with  $\varepsilon$ -independent local model potentials are often somewhat unsatisfactory, and it

has been shown that they can be corrected by  $\varepsilon$ -dependent model potentials [16]. The differences are much larger with Li, Cs, Zn, Hg than with Na, K. The former atoms are just those for which the  $l$ -dependency of the effective potential – that is the nonlocality – is much more pronounced than for Na, K, Mg [5]. Thus it might be possible and would be more natural to attribute the differences mentioned to the neglect of the  $l$ -dependency in the model potential.

Concluding, with regard to the rather nice results obtained so far with simple model potentials  $V^{\nu}(x)$  (e.g. [1, 3–5, 17]), it seems questionable whether it is really necessary to use energy-dependent model potentials.

### References

1. A nice review on pseudopotential theory is given by Weeks, J. D., Hazi, A., Rice, S. A.: *Advances physic. Chem.* **15**, 283 (1969); see too Austin, B. J., Heine, V., Sham, L. J.: *Physic. Rev.* **127**, 276 (1962).
2. Schwarz, W. H. E.: *Theoret. chim. Acta (Berl.)* **11**, 307 (1968).
3. Szasz, L., McGinn, G.: *J. chem. Physics* **47**, 3495 (1967).
4. Schwarz, W. H. E.: *Acta physica hung.* **27**, 391 (1969); *Theoret. chim. Acta (Berl.)* **11**, 377 (1968).
5. — *Theoret. chim. Acta (Berl.)* **15**, 235 (1969); *Chem. Physics Letters* **10**, in press (1971).
6. — *J. chem. Physics* **55**, in press (1971).
7. Austin, B. J., Heine, V., Sham, L. J.: *Physic. Rev.* **127**, 276 (1962).
8. Heine, V.: *Solid State Physics* **24**, 21, 27 (1970).
9. Logatchov, Y. A.: *Physica Status solidi* **25**, 763 (1968).
10. Cohen, M. H., Heine, V.: *Physic. Rev.* **122**, 1821 (1961); Schlosser, H.: *J. chem. Physics* **53**, 4035 (1970).
11. Hellmann, H.: *Acta physicochim. URSS* **1**, 913 (1935); **4**, 225, 324 (1936).
12. Shaw, R. W., Harrison, W. A.: *Physic. Rev.* **163**, 604 (1967).
13. Abarenkow, I. V., Heine, V.: *Philos. Mag. (Ser. 8)* **12**, 529 (1965); Abarenkow, I. V., Antonova, I. M.: *Physica Status solidi* **20**, 643 (1967).
14. Schneider, B., Weinberg, M., Tully, J., Berry, R. S.: *Physic. Rev.* **182**, 133 (1969).
15. Bardsley, J. N., Dorn, N. P.: *Sixth Int. Conf. Phys. El. Atom. Coll.* p. 43. Cambridge (Mass.): MIT Press 1969; Bardsley, J. N.: *Chem. Physics Letters* **7**, 517 (1970).
16. Ashcroft, N. W.: *J. Physics C* **1**, 232 (1968); Evans, R., Greenwood, D. A., Lloyd, P., Ziman, J. M.: *Physic. Letters* **30 A**, 313 (1969).
17. Giuliano, E. S., Ruggeri, R.: *Nuovo Cimento* **61 B**, 53 (1969); Koch, R. J., Kutzelnigg, W., Bingel, W. A.: *Chem. Physics Letters* **2**, 197 (1968); – *Acta physica hung.* **27**, 323 (1969); Kutzelnigg, W.: *Chem. Physics Letters* **4**, 435 (1969).

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