

A new approach is presented to constructing the true effective valency Hamiltonian for a molecular system, which is based on a quasiparticle description. The binding energy and self-consistent field potential are calculated via the effective valency-electron interaction. Valency-state energy calculations have been performed for neon-type highly ionized atoms, where the examples taken are Cl VIII and the potential curve for the $X^1\Sigma^+$ state of HF, in addition to the spectroscopic factors for various atoms and ions.

Nonempirical molecular-calculation methods are widely accompanied by various semiempirical theories [1], and such methods are thus applicable to many aspects of theoretical chemistry. On the other hand, there are various problems in the semiempirical theory, particularly ones associated with the various parametrization schemes. The number of parameters involved increases further when these methods are applied to any system containing several atoms from different elements such as transition ones. Also, the application ranges for these theories are usually restricted. There is a need for improved parameterization and reliable prediction from the theories, which has led to new developments. The problem over the various theories could be resolved if one could find the form for the true effective valency Hamiltonian for a molecule that reproduces the potential surfaces for any valency state precisely.

At present, there are various model expressions for H_{eff}^V , which are derived by various techniques, including by means of projection operators, van Vleck transformations, multiparticle perturbation theory, or the Bloch-de Cloiseaux quasi-degenerate-state perturbation theory, etc. [1]. In the latter forms, H_{eff}^V is a poor theoretical Hamiltonian, which is modified by the corrections in the perturbation-theory series for the total H. Higher-order corrections are required to give the needed accuracy. As a rule, it is laborious to calculate those terms.

Here I propose a new approach to constructing H_{eff}^V , which is based on a quasiparticle description, where I consider calculating bond energies and self-consistent field potentials, which appear in H_{eff}^V , in terms of the effective valency-electron interaction; some applications are discussed.

EFFECTIVE QUASIPARTICLE VALENCY LAGRANGIAN

The quasiparticle formalism in Fermi liquid theory [2, 3] involves converting from the actual system $N = N_C + N_V$ of interacting electrons in the molecule (where N_C and N_V are the numbers of core and valency electrons) to a system of N quasiparticles having an effective pair interaction with an unambiguous relationship to the quasiparticle scattering amplitude near the Fermi surface. The quasiparticle equations of motion follow from Dyson's equation when the mass operator Σ is expanded near the Fermi surface as a series in powers of $\varepsilon - \varepsilon_F$, $p^2 - p_F^2$ (atomic units are used):

$$H_{\text{eff}}\psi_\lambda(r) \equiv [\varepsilon_p + \Sigma_0(r) + p\Sigma_1(r)p + \varepsilon_\lambda\Sigma_2(r)]\psi_\lambda(r) = \varepsilon_\lambda\psi_\lambda(r), \quad (1)$$

in which $\varepsilon_p = \frac{p^2}{2} - \frac{\sum_\alpha Z_\alpha}{r}$ (α enumerates the nuclei in the molecule), and ψ_λ is the quasiparticle wave function, which is orthonormalized with weight

$$\int \psi_\lambda^*(r) [1 - \Sigma_2(r)] \psi_{\lambda'}(r) dr = \delta_{\lambda\lambda'},$$

in which Σ_i are the components of the mass operator Σ_q , which are determined as the variational derivatives of the quasiparticle Lagrangian L_q (see below). The basic task is to construct L_q , which has a standard relation to H_{eff}^V . We construct L_q such that the Lagrange equations coincide with (1) for the valency states. These equations can be derived by means of a variational principle starting from L_q , which must be determined as a quasiparticle-density functional [4]:

$$\begin{aligned} v_0 &= \sum_{\lambda} n_{\lambda} |\psi_{\lambda}|^2, \\ v_1 &= \frac{1}{2} \sum_{\lambda} n_{\lambda} |\nabla \psi_{\lambda}|^2, \\ v_2 &= \frac{1}{2i} \sum_{\lambda} n_{\lambda} [\dot{\psi}_{\lambda}^* \psi_{\lambda} - \psi_{\lambda}^* \dot{\psi}_{\lambda}]. \end{aligned} \quad (2)$$

The densities v_0 and v_1 are analogous to the Hartree-Fock electron density ρ ($\rho = v_0 a$) and the kinetic-energy density correspondingly; v_2 does not have an analog in Hartree-Fock theory and appears on account of incorporating the energy dependence for Σ_q . We write L_q as $L_q = L_q^0 + L_q^1$, where the free Lagrangian L_q^0 has the standard form

$$L_q^0 = \int dr \sum_{\lambda} n_{\lambda} \psi_{\lambda}^* \left(i \frac{\partial}{\partial t} - \varepsilon_p \right) \psi_{\lambda}, \quad (3)$$

and the interaction Lagrangian L_q^1 is defined by

$$L_q^1 = L_k - \frac{1}{2} \sum_{i,k=0}^2 \int \beta_{ik} F(r_1 r_2) v_i(r_1) v_k(r_2) dr_1 dr_2. \quad (4)$$

Here F is the effective polarization-interaction potential, while β_{ik} are constants; the Coulomb term L_k takes the form

$$L_k = -\frac{1}{2} \int [1 - \Sigma_2(r_1)] v_0(r_1) [1 - \Sigma_2(r_2)] v_0(r_2) / |r_1 - r_2| dr_1 dr_2. \quad (5)$$

In the simplest approximation, F is determined from the correlation pseudopotential V_c :

$$F(r_1 r_2) = \delta V_c / \delta v_0 \cdot \delta(r_1 - r_2). \quad (6)$$

A rigorous expression for F has been derived recently [5, 6] from calculations on the corresponding perturbation-theory polarization diagrams of Rayleigh-Schrödinger type. We use (4)-(6) to get as follows [3] for $\Sigma_i = -\delta L_q^1 / \delta v_{ik}$

$$\begin{aligned} \Sigma_0 &= (1 - \Sigma_2) V_k + \Sigma_0^{\text{ex}} + \frac{1}{2} \beta_{00} \frac{\delta^2 V_c}{\delta v_0^2} v_0^2 + \beta_{00} \frac{\delta V_c}{\delta v_0} v_0 + \beta_{01} \frac{\delta V_c}{\delta v_0} v_1 + \\ &\quad \beta_{01} \frac{\delta^2 V_c}{\delta v_0^2} v_0 v_1 + \beta_{02} \frac{\delta^2 V_c}{\delta v_0^2} v_0 v_2 + \beta_{02} \frac{\delta V_c}{\delta v_0} v_2; \\ \Sigma_1 &= \beta_{01} \frac{\delta V_c}{\delta v_0} v_0 + \beta_{12} \frac{\delta V_c}{\delta v_0} v_2 + \beta_{11} \frac{\delta V_c}{\delta v_0} v_1; \\ \Sigma_2 &= \beta_{02} \frac{\delta V_c}{\delta v_0} v_0 + \beta_{12} \frac{\delta V_c}{\delta v_0} v_1 + \beta_{22} \frac{\delta V_c}{\delta v_0} v_2, \end{aligned} \quad (7)$$

where Σ_0^{ex} is the exchange term and V_k is the Coulomb potential [see (5)].

We obtain an explicit expression for H_{eff}^V . We use the $H_{\text{eff}} = \dot{\psi}_{\lambda}^* \frac{\delta L_q}{\delta \psi_{\lambda}^*} + \dot{\psi}_{\lambda} \frac{\delta L_q}{\delta \psi_{\lambda}} - L_q$, and after simple calculations get H_{eff} as

$$H_{\text{eff}} = H_q^0 + H_q' = H_q^0 - L_k + \frac{1}{2} \beta_{00} \frac{\delta V_c}{\delta v_0} v_0^2 + \beta_{01} \frac{\delta V_c}{\delta v_0} v_0 v_1 + \frac{1}{2} \beta_{11} \frac{\delta V_c}{\delta v_0} v_1^2 - \frac{1}{2} \beta_{22} \frac{\delta V_c}{\delta v_0} v_2^2. \quad (8)$$

One needs to consider the β_{ik} to determine H_{eff} completely.

QUASIPARTICLE SEMIEMPIRICAL-THEORY CONSTANTS

Σ_1 arises because of delay effects, whose contribution to the total energy is negligible, so one can put $\beta_{01} = \beta_{11} = \beta_{12} = 0$. As the $\Sigma_2(\beta_{22})$ terms are also obviously small, we further assume $\beta_{22} = 0$. The value of β_{00} is dependent to certain extent on the correctness in determining V_c . If we introduce the renormalized pseudopotential $V_c^{\text{r}} = \beta_{00}V_c$ and take one of the correct correlation pseudopotentials in density-functional theory as it, we can put $\beta_{00} = 1$ without loss of generality. We determine the energy-dependence constant from information on the spectroscopic factors \mathcal{F} , extracted from the ionization cross sections. The relation between β_{02} and \mathcal{F} is [7]

$$\beta_{02} = (1 - \mathcal{F}^{-1}) / \left[\delta V_c / \delta v_0 \Big|_{v_0=v_0^0} \right], \quad (9)$$

in which $v_0^0 = v_0(0)$. One could use the normal conditions applied in semiempirical theory to determine β_{ik} , which for example for π -electron molecular systems take the form

$$\langle \Delta_k | H_{\text{eff}}^v | \Delta_k \rangle = E_c + \sum_{v_j < k} \alpha_j + \frac{1}{2} \sum_{v_i \neq v_j < k} \gamma_{ij},$$

where E_c is the core energy, Δ_k is a linear combination of Slater determinants composed of valency orbitals $\{v\}$, and α and γ are the usual semiempirical values for the Coulomb integral α_i and the electron-electron repulsion integral γ_{ij} . From L_q , one can readily derive the quasiparticle scattering amplitude at the potential function Γ [3]. For small transferred momenta q , one can distinguish a block U from the set of Γ graphs that cannot be split up into parts joined by two lines on the particle-hole channel: $\Gamma = U + \text{UGGF}$ (G is a Green's function). There is a substantial q dependence for those graphs in Γ that contain two lines each (particles and holes), and as there are none such in block U , then for small values of q it can be replaced by one that is the same for all molecules, i.e., by a universal constant. One can avoid the integration over the region remote from the potential surface present in the UGGF term by means of Landau's renormalization procedure [2], which involves the assumption that U has no singularities for $q \rightarrow 0$. That assumption is naturally violated for Coulomb interaction, so the procedure for constructing L_q and Γ requires refinement: first one should distinguish the Coulomb interaction, after which the remaining part of L_q is parametrized by means of universal constants. This scheme has in fact been implemented above.

RELATION BETWEEN THE QUASIPARTICLE METHOD OF DERIVING H^v AND THE PROJECTION-OPERATOR METHOD

For convenience, we transfer to matrix notation. We represent the exact wave function as $\psi = \Phi + X$, where Φ is a linear combination of Slater determinants $\{\Delta_k\}$ composed of the valency MO $\{v\}$, while X is defined as a superposition of all the other determinants formed as a result of introducing the complete set of excited orbitals $\{e\}$ along with the $\{v\}$ MO and the core MO $\{c\}$. We represent Φ and X as expansions in terms of the individual configurations:

$$\Phi = \sum_k C_k \Delta_k, \quad X = \sum_L C_L \Omega_L. \quad (10)$$

We substitute (5), (8), and (10) into the Schrödinger equation:

$$\begin{aligned} \sum_k \langle \Delta_{k'} | H_{\text{eff}} | \Delta_k \rangle C_k &= EC_k \equiv \sum_{k'} [\langle \Delta_{k'} | H_{\text{st}} | \Delta_k \rangle + \langle \Delta_{k'} | H_c | \Delta_k \rangle] C_k + \\ &+ \sum_L \langle \Delta_{k'} | H_{\text{st}} | \Delta_L \rangle C_L + \sum_L \langle \Delta_{k'} | H_c | \Delta_L \rangle C_L, \end{aligned} \quad (11)$$

in which H_{st} is the standard molecular Hamiltonian, while

$$H_c = \frac{1}{2} \beta_{00} \frac{\delta V_c}{\delta v_0} - 2\beta_{02} \frac{\delta V_c}{\delta v_0} \frac{v_0}{|r_1 - r_2|} + \beta_{02}^2 \left(\frac{\delta V_c}{\delta v_0} \right)^2 \frac{v_0^2}{|r_1 - r_2|}.$$

(11) in matrix form is

$$H_{\text{eff}}C_p = (H_{\text{ppst}} + H_{\text{ppc}})C_p + (H_{\text{pqst}} + H_{\text{pqc}})C_q \equiv EC_p. \quad (12)$$

We compare (12) with the analogous equation in the projection-operator method [1] to get

$$H_{\text{pq}}(El_q - H_{\text{qq}})^{-1}H_{\text{qp}}C_p = H_{\text{ppc}}C_p + (H_{\text{pqst}} + H_{\text{pqc}})C_q. \quad (13)$$

Here ℓ is unit matrix in the Ω_L function space (q is a block). To simplify the calculations, H_c can be renormalized in such a way that

$$H_{\text{ppc}}C_p + (H_{\text{pqst}} + H_{\text{pqc}})C_q = \tilde{H}_{\text{ppc}}C_p,$$

so instead of (12) we get

$$(H_{\text{ppst}} + \tilde{H}_{\text{ppc}})C_p = EC_p.$$

This HV derivation gives a physically more definite Hamiltonian than do existing methods. A feature of the (8) H_{eff}^V is that the energy dependence is explicitly incorporated. Previously, forms have been suggested that are not explicitly dependent on the energy. Such forms require $(El_q - H_{\text{qq}})^{-1}$ in (13) to be expanded as a series around a certain energy. Calculating the energy-dependence corrections for such a series involves some computational difficulties, which are absent in the quasiparticle approach. As $H(E)$ varies slowly in the range in E for the valency states, this enables one to determine rapidly whether the valency shell has been chosen correctly. If the determination is incorrect, one should expand the derivation and derive a new H^V slightly dependent on E in a particular E range. The true H_{eff}^V shows transferability for the main parts in HV between related molecules. We specify β_{ik} in (8) to get a unique H_{eff} dependent on E , which is the same for related molecules, e.g., for any π -electron system containing six π electrons.

SOME APPLICATIONS

We consider excited states of Ne-type highly ionized atoms, in particular Cl VIII. These represent a major application, because Ne-type ions are very important in applications (see reviews [8, 9]). A low-lying excited state is formed on the excitation of a 2s or 2p electron from the ground-state $1s^22s^22p^6$ configuration (core), which results in a 3 ℓ electron above it, and a 2 ℓ vacancy in the core. To determine the energy of such a state, one has to calculate the eigenvalues of H_{eff}^V for the two-quasiparticle system (3 ℓ electron and 2 ℓ hole in the relativistic approximation). It is essential to incorporate relativistic effects for highly ionized atoms. We decompose H_{eff}^V into the zeroth-approximation Hamiltonian

$$H_{\text{eff}}^{V0} = \sum_{i=1}^2 h_i^D + \int dr' \rho_c(r')/|r - r'| + (3/8\pi)^{1/3} \rho_c^{1/3}(r),$$

in which h_i^D is the one-particle Dirac Hamiltonian and ρ_c is the core density, for which we use a hydrogen-type approximation with an effective screening parameter [5]; there is also the perturbation Hamiltonian

$$V_{\text{eff}}^V = \frac{1}{|r_1 - r_2|} + \beta_{00}F(r_1, r_2) - \frac{1}{2} \int dr' \rho_c(r')/|r_1 - r'| - \frac{1}{2} \int dr' \rho_c(r')/|r' - r_2|.$$

We take the potential F as [5]

$$\beta_{00}F(r_1, r_2) = X \left\{ \int dr' \rho_c^{1/3}(r')/|r_1 - r'| \cdot |r' - r_2| - \left[\int dr' \rho_c^{1/3}(r')/|r_1 - r'| \cdot \int dr' \rho_c^{1/3}(r')/|r' - r_2| \right] / \int dr' \rho_c^{1/3}(r) \right\},$$

TABLE 1. Transition Energies in Cl VIII (eV) Reckoned from the Ground-State Energy

Conformation	Term	Calculation	Experiment	Conformation	Term	Calculation	Experiment	
2p3s	3P_2	208,84	208,79	2p3d	3P_0	244,42	244,43	
	3P_1	209,54	209,47		3P_1	244,61	244,62	
	3P_0	210,49	210,47		3P_2	245,01	245,02	
	1P_1	211,43	211,33		3F_4	245,44	245,40	
	3S_1	222,43	222,28		3F_3	245,79	245,70	
	3D_3	224,56	224,57		3F_2	246,29	246,23	
	3D_2	224,73	224,72		1F_3	246,81	246,62	
	3D_1	225,28	225,30		3D_1	247,77	247,66	
	2p3p	3P_2	225,89		225,91	3D_2	248,08	248,02
		3P_1	227,14		227,21	3D_3	248,05	247,95
3P_0		226,85	226,89	1D_2	247,81	247,73		
1P_1		226,49	226,52	1P_1	251,54	250,59		
1D_2		227,03	227,06	2s3s	3S_1	278,39		
1S_0		235,54	234,76		1S_0	281,46		
2s3p		3P_0	293,90		2s3d	3D_1	314,545	
		3P_1	293,98	294,04		3D_2	314,548	
	3P_2	294,18		3D_3		314,554		
	1P_1	295,25	297,79	1D_2		316,352		

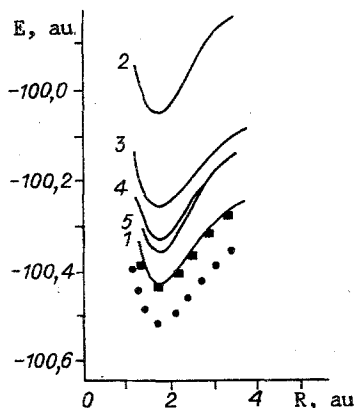


Fig. 1. Potential curves for the $X^1\Sigma^+$ state in HF calculated: 1) here; 2) by the Hartree-Fock method; 3) by the generalized valency-bond method; 4) from the coupled electron pair method; 5) from multiparticle perturbation theory with zeroth-approximation Hartree-Fock treatment (■ and ● from experiment).

where X is a numerical coefficient. This F enables one to incorporate correctly an important second-order perturbation-theory effect: the polarization interaction between the quasiparticles via the core. Another second-order effect is quasiparticle mutual screening, which is incorporated by adding the screening potential to $H_{\text{eff}}^{\text{V}0}$ and subtracting it from $V_{\text{eff}}^{\text{V}}$:

$$W(r|g) = g(3 + gr)/Z(3 + 2gr + 2g^2r^2),$$

in which $g = Z/n^2(Z + N_c)$. The computational procedure has been described in detail in [5]. Table 1 gives calculated energies for the $2s^22p^53s$, $3p$, $3d$, and $2s2p^63s$, $3p$, $3d$ states of Cl VIII together with measurements [10]. Another application is the energy of the $X^1\Sigma^+$ ground state for HF. The bond here is formed by a pair of shared electrons, which are considered as quasiparticles against the background of the other core electrons. One averages $H_{\text{eff}}^{\text{V}}$ on the standard Heitler-London molecular wave functions composed of the AO ψ_i to give the bond energy ΔE as [11]

$$\begin{aligned} \Delta E = & Z_a^{\text{CO}} Z_b^{\text{CO}} / R - \int \psi_a^2 Z_a^* / r_a d\tau - \left[\int \psi_a \psi_b d\tau \right] \times \\ & \int \psi_a \left(\frac{Z_a^*}{r_a} + \frac{Z_b^*}{r_b} \right) \psi_b d\tau - \int \psi_b^2 Z_a^* / r_a d\tau + \\ & \int \int \psi_a^2(1) \left[\frac{1}{|r_1 - r_2|} + \beta_{00} F(r_1 r_2) \right] \psi_b^2(2) d\tau_1 d\tau_2. \end{aligned}$$

TABLE 2. Spectroscopic Factors for Atoms and Ions

Atom	Shell	F	Ion	Shell	F
Xe	5s ²	0,34*	Cl ⁻	3s ²	0,70
Kr	4s ²	0,46	K ⁺	3s ²	0,66
Ar	3s ²	0,68	Ca ⁺⁺	3s ²	0,64

*Exact value.

We take the effective potential for the exchange-correlation interaction [11] as F:

$$\beta_{00}F(r_1r_2) = C\delta(r_1 - r_2) / \left[\int \psi_a^2 \psi_b^2 d\tau \right]^{2/3},$$

in which $C = 3(3/8\pi)^{1/3}\alpha\beta$ and α is the parameter in the X_α theory, while β is function of the internuclear distance R , which is dependent parametrically on the atomic radii R_a and R_b [12]:

$$\beta(R) = \gamma \exp[(R_a + R_b - 2R)/(2Z_a^* + 2Z_b^*)].$$

The effective molecular charges Z^{CO} and Z^* together with the empirical parameter γ have been determined by the method described in detail in [11] (see also [12]). We merely note that γ is found from the condition for correct bond-characteristic description for the group of diatomic hydrides AH ($A = H - F$), in particular HF: $\gamma = \exp(-0.6 - R)$. As ψ we took Slater AO with the exponents from [13]. Figure 1 shows our calculated potential curve for $X^1\Sigma^+HF$ (curve 1) together with the curves calculated from the Hartree-Fock method (curve 2), the valency-bond method (curve 3), and the coupled electron-pair method (curve 4), in addition to perturbation theory with zeroth-approximation Hartree-Fock treatment (curve 5), and the observed curve [14]. Effective correlation incorporation gives agreement between theory and experiment better than that with the other and more complicated methods. A natural application is to calculations on spectroscopic factors for atoms and molecules, as information on these is important for example in fast-electron scattering [7]. We use (9) and take V_c as the Gunnarsson-Lundqvist potential [15] to get the spectroscopic factor as

$$\mathcal{F} = \left[1 - \beta_{02} \frac{\delta V_c}{\delta v_0} \Big|_{v_0=v_0^0} \cdot v_0^0 \right]^{-1} \approx \left[1 - \beta_{02} \frac{\delta V_c}{\delta \rho} \Big|_{\rho=\rho(0)} \cdot \rho(0) \right]^{-1}, \quad (14)$$

in which $\delta V_c / \delta \rho = 0.3283\rho^{-2/3} + 0.20398\rho^{-2/3} / (1 + 18.3767\rho^{1/3})$. We calibrate the universal constant β_{02} from the exact value of F, and in particular we take the spectroscopic factor for the 5s² shell in Xe: $\mathcal{F}_{Xe} = 0.34$ [16]. We use Hartree-Fock ρ [17] to get from (14) that $\beta_{02} = -0.47$. Table 2 gives calculations on spectroscopic factors for various atoms. A separate paper deals with applications to ionization cross sections, molecular oscillator strengths, advancing Fermi-surface quasiparticle theory, and a new form of the CNDO method. I am indebted to L. N. Ivanov and E. P. Ivanova for valuable advice.

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